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ON THE PETROLOGICAL, GEOCHEMICAL, AND GEOPHYSICAL CHARACTERIZATION OF A RETURNED MARS SURFACE SAMPLE AND THE IMPACT OF BIOLOGICAL STERILIZATION ON THE ANALYSES

April 1974

(NASA-TM-X-72501) ON THE PETROLOGICAL, GEOCHEMICAL, AND GEOPHYSICAL CHARACTERIZATION OF A RETURNED MARS SURFACE SAMPLE AND THE IMPACT OF BIOLOGICAL STERILIZATION ON THE ANALYSES (NASA) 387 p G3/91

N75-31982

Unclas
17984

National Aeronautics and Space Administration

LYNDON B. JOHNSON SPACE CENTER

Houston, Texas

ON THE PETROLOGICAL, GEOCHEMICAL, AND GEOPHYSICAL CHARACTERIZATION

OF A RETURNED MARS SURFACE SAMPLE

AND THE IMPACT OF BIOLOGICAL STERILIZATION ON THE ANALYSES

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INTRODUCTION

The analysis of returned lunar samples has advanced our understanding of the formation and evolution of the Moon in a way that could not otherwise have been achieved. Studies of the returned lunar materials have provided a baseline of "ground-truth" which past and future observations by remote methods can normalize to and which theoretical interpretations must respect. Return of a sample from the planet Mars would be another vital landmark in the characterization of the nature and history of development of bodies within the solar system.

This report has the following purposes: to identify those experiments that could and should be done on a returned Martian sample in order to characterize its inorganic properties; to evaluate, insofar as can be done, the effects of potential biological sterilization of the sample by heating prior to its return; to identify particular analytical techniques needing further improvement in order to make optimum use of a returned sample; and to identify experiments to be done on simulants, with and without sterilization, that better define the limits of information available about the planet from analyses of returned samples.

In order to meet those purposes with accuracy and authority in the short time available, the following procedure was used. A general outline for the study was prepared by five members of the Planetary and Earth Sciences Division, Johnson Space Center, who solicited the advice of a broad range of other scientists whose expertise would contribute to experiment definition and to the evaluation of effects of biological sterilization. Excellent cooperation was received from the scientific community, owing to the great interest in and enthusiasm for the proposed Martian sample return. Many scientists sent letters discussing experiments and problems in their particular areas of expertise. Their letters are included as Appendix II of this report. These letters were heavily relied on in constructing the body of the report, but the seriously concerned reader will find much additional information of value in them.

Soon after the deadline for receipt of such letters was past, a committee of scientists was assembled to write this report. For this purpose, a meeting was held on March 27-28, 1974, at the Lunar Science Institute near Houston, Texas. Members of the committee and their affiliations are as follows: S. O. Agrell, Cambridge Univ.; D. D. Bogard, NASA Johnson Space Center (JSC); R. Brett, JSC; S. Chang, NASA Ames Research Center; H. P. Eugster, Johns Hopkins Univ.; E. K. Gibson, JSC; L. A. Haskin, Chairman, JSC; J. Huneke, Calif. Inst. Technol.; E. A. King, Univ. of Houston; L. E. Nyquist, JSC; W. C. Phinney, JSC; D. Strangway, Univ. of Toronto; H. P. Taylor, Calif. Inst. Technology; S. R. Taylor, Australian Nat. Univ. and Lunar Science Inst.; and J. Warner, JSC. During part of the meeting, R. S. Young, NASA Headquarters, and M. B. Duke, JSC were also present.

This report is structured as follows: (a) the introduction, (b) four separate, more or less self-contained experimental sections, each prepared by a separate subcommittee, (c) a summary of the more general conclusions reached by the group in regard to the importance of the proposed mission, sampling procedures, sample containers, some anticipated consequences of sterilizations, and recommendations for work to be done prior to the mission.

Somewhat independently, but concurrently with this study, a series of experiments on the effects of heating was done in a number of laboratories. These experiments were organized by E. A. King, Univ. of Houston. The results of this study are given as Appendix III of this report.

MINERALOGY - PETROLOGY

A. Basic Data and Importance

The most fundamental data needed for the interpretation of the mineralogy and petrology of Mars are the identities of the mineral species and rock types present in returned samples. Other features that must be described and documented include particle size, shape, inclusions, surface features, and other characteristics that will yield information on surface processes and sample history throughout the evolution of the planet. This must be an exhaustive study that will involve every returned grain and fragment that can be made available. The primary mineralogy has obvious relevance to such fundamental problems as the degree of planetary differentiation and the geologic history of the Martian surface and interior. Volcanic activity and its depth of origin, sedimentary deposits and their transport mechanism, metamorphic products and their temperatures, pressures, and fugacities of origin are among the typical problems. Secondary mineralogy may result from surface-related mineral growth and phase changes during the chemical alteration processes that have occurred on the Martian surface through time. Another important aspect of the planet's history, the record of any living matter, would be preserved in fossil assemblages which could be encountered during mineralogic and petrologic studies. In interpreting petrographic data, care would have to be taken to identify mineralogical changes resulting from any sample sterilization, which could obscure certain features of primary and secondary mineralogy.

B. Techniques of Study

The techniques recommended for the collection of the basic data on the mineralogy and petrology of Mars include the following:

1. Petrographic Microscope

   As with terrestrial and lunar rocks and mineral grains, it is anticipated that the examination of polished thin sections of rocks and grain mounts in both transmitted and reflected light will provide many of the required mineralogical and petrological data. In addition to mineral identities and textural data, inclusions (see data from Roedder, Appendix II), fine exsolution phases, structural imperfections, and perhaps fossils can be studied.

2. X-Ray Diffraction

   The film camera techniques are a powerful method for the identification of individual grains. These may be rotated on a fiber or remounted in several orientations in a Debye-Scherrer camera

or illuminated in a Gandolfi camera for generation of fairly complete diffraction patterns. Bulk dust samples of several milligrams can be examined in a preliminary manner by ordinary powder diffractometry or spindle Debye-Scherrer techniques.

3. Electron Microprobe

The composition and zoning of individual grains in rock fragments and grain mounts obtained from polished thin sections by this technique will be an essential part of the data required. In addition, the "defocused beam" method can give good analytical data for the composition of rock fragments if the mean grain size is sufficiently small.

4. Scanning Electron Microscope (SEM)

This technique will be especially valuable for the chemical analysis and identification of very small grains in the Mars sample. It will also provide excellent documentation of particle size, shape, and surface characteristics, especially for the very fine fraction of the sample. In addition, it may allow recognition and characterization of microfossils.

5. Transmission Electron Microscopy (TEM)

This is the only presently available technique that can detect and characterize ultrafine intergrowths and inclusions in mineral grains and glasses. These data, coupled with optical microscope examinations, can provide identifications and characterizations of mineral grains, glasses, and their inclusions and intergrowths at many size scales.

6. Ion Probe

We anticipate that this instrument should be a standard petrographic tool by the early 1980's for the broad chemical and isotopic analysis of small fragments and individual mineral grains.

7. Electron Surface Chemical Analysis (ESCA)

Surface coatings and thin mineral deposits on individual grains and rock fragments may be sensitive indicators of the physical and chemical processes that have occurred at or near the Martian surface. Although the SEM and electron microprobe may yield some data on these coatings and thin films, sensitive electron analysis techniques likely will be required for the very thin deposits.

8. Mössbauer Spectroscopy

This technique can be used for mineral identification of bulk samples. It also provides crystallochemical data on individual

mineral phases and is especially useful when used in conjunction with x-ray diffraction data.

9. Differential Thermal Analysis/Thermogravimetric Analysis/Effluent Gas Analysis

   These methods will be invaluable in identifying and characterizing minerals present in small aliquots of the bulk sample, as well as in establishing the amounts and identities of volatile components driven out of the samples at various temperatures.

10. Absorption and Reflection Spectroscopy

    The bulk sample as well as individual mineral grains should be characterized by these techniques. Over a wide portion of the spectrum, these methods provide data on valence states and structural position of various elements and functional groups in different mineral phases.

The above list is not comprehensive but serves to identify the main techniques that would be used for mineralogical and petrological characterization of the sample. New techniques probably will be developed and old methods drastically improved before the sample is available.

In the event that the returned sample were composed largely of particulate regolith, as we now anticipate, the goal of many of the individual grain and particle studies will be to identify populations of particles that have had different origins and histories. This will allow a broader interpretation of the sample than mere bulk analyses. We have good reasons to expect that much of the material will be very fine grained; the task of analyzing such material grain by grain is immense. A substantial effort to improve techniques of handling and analysis for very fine (< 10μm) and ultra fine (< 1μm) grains would prove extremely valuable (not only for work on the proposed Martian sample but for lunar and terrestrial studies as well).

C. Nature of Petrologic Problems

On Mars we may expect to find two sources of rock material: endogenous rocks ranging from igneous to sedimentary, and a small proportion of impact-produced rocks associated with minor amounts of exogenous material of meteoritic origin.

The primary igneous rocks may have a wide range of compositions and may occur in states ranging from slowly cooled to quenched. The igneous rocks should consist predominantly of anhydrous minerals of high temperature origin; e.g., olivines, pyroxenes, feldspars, silica minerals, and possibly amphiboles and micas. These rocks may locally be

subject to fumarolic or hydrothermal activity where secondary minerals such as oxides, sulfides, halides, hydroxides, and zeolites may have developed.

Because Mars has an atmosphere containing both H_2O and CO_2, we must consider the possibility of hydrates and carbonates in both the primary mineral matter and possible weathering products. Because the humidity is much lower on Mars than on Earth, chemical weathering may not occur primarily on the Martian surface, but rather at some shallow depth where permafrost or liquid water may occur.

Weathering processes on Mars are likely to be both chemical and mechanical. They may include redistribution of original secondary minerals and generation of new secondary minerals; e.g., clay minerals, carbonates (especially alkali carbonates such as Dawsonite or Nahcolite), halides, sulfates, hydroxides.

In addition to single mineral (or phase) particles, four types of polyphase particles are expected; these are igneous rock fragments, sedimentary rock fragments, particles with external reaction zones, and particles with coatings. The mineral-mineral relations, both of an equilibrium and a reaction nature, that are preserved in these types of particles are the most important types of data for deducing Martian rock-forming processes and inferring the nature of inaccessible regions of the planet.

There are three broad questions on which the study of polyphase particles may bear:

1. What are the Primary Martian Plutonic and Volcanic Rocks?

   The answers to this question will yield information about the Martian interior. The nature of the source regions of the partial melts that crystallized into basalts may be deduced from the mineralogy of the basalts. Sampled suites of plutonic rocks (that crystallized at depth) may be used to deduce the nature of any major Martian internal differentiation. Heterogeneous equilibria in plutonic and volcanic rocks are capable of yielding information concerning the intensive parameters of the Martian interior, including T, P, and oxidation state. Finally, gases and liquids trapped as inclusions in these rocks yield direct data concerning volatiles in the Martian interior.

   There are two approaches to understanding plutonic and volcanic rocks. The first, and least satisfactory, is to infer the types of plutonic and volcanic rocks from individual mineral grains. A much more rigorous approach is to describe igneous rock fragments systematically. Our lunar experience has shown that petrographic descriptions adequate for such purposes can be obtained

from rock fragments as small as 5 times the mean grain size. This concept dictates that in studying the returned sample each fragment of igneous rock should be treated as a rock, and each of its constituent minerals studied in relation to the other minerals present.

2. What are the Martian Surface Processes of Erosion and Weathering?

   Polyphase particles that are sedimentary lithic fragments will have been produced by erosion. Hence, systematic study of those particles will help to identify processes of chemical and mechanical erosion. Much information is gained by comparing sediments with igneous rocks; i.e., comparing the primary minerals to their products from weathering. Polyphase fragments that display external reaction zones preserve both the products of weathering reactions and their primary mineral parents so that their association is unambiguous. Such particles would be particularly useful, since some components of the Martian atmosphere might be deduced with moderate precision from their study.

3. What is the Composition of the Transient or Permanent Martian Atmosphere?

   Polyphase particles with reaction zones, as outlined above, may be used to provide information on this problem. In addition, there might be polyphase fragments with mineral coatings (even thin films such as the Zn- and Pb-rich film on the orange lunar glass of Apollo 17). The atmosphere may contain components that reach saturation and precipitate onto rock fragments. These components may come from volcanic emanations or be true atmospheric gases. The zone of saturation, if any, might be right on the Martian surface or at some distance below the surface.

D. Sample Acquisition and Supporting Data

We cannot envision any returned Mars sample whose study would not add greatly to our knowledge and understanding of that planet as well as the Solar System. On the other hand, judicious selection and processing of the sample during acquisition may enormously enhance its scientific value. Experience with both lunar and terrestrial rocks has shown that particles greater than about 2mm in diameter are required to yield sufficient textural and petrographic detail to permit truly fruitful petrologic interpretation, even if the rocks are texturally quite fine-grained. On the other hand, very large fragments (greater than several centimeters in diameter) are often wasteful of sample mass, in terms of information return. Because we regard the petrographic characterization of Martian rocks as particularly important (albeit difficult to achieve by remotely operated instruments), we

recommend that the sample-acquisition mechanism have the capability to ensure the delivery of material enriched in 2-20 mm diameter fragments in addition to a substantial sample of fines material. This might be accomplished by a sieving or raking device similar to those used on the lunar surface.

The keys to many important questions regarding near-surface processes and the recent erosional-depositional history of Mars may lie in the fine-grained stratigraphy of the surface materials. The mode of collection most likely to preserve any layering sufficiently well to permit stratigraphic studies is coring. Collection of a 1-meter long core would thus provide a very interesting sample.

It would be desirable to collect a variety of subsamples from different regions and different depths in the immediate vicinity of the lander and, if possible, to maintain these samples separate from one another. One possible mechanism for accomplishing this might be a scoop-type sampler similar to that to be used on Viking '75. This capability helps to ensure the acquisition of a useful sample even if material that can be sampled is but sparsely and erratically distributed in the sampler field. Used in conjunction with an imaging system, such a sampler would permit some selection of sample characteristics that might enhance scientific return.

Although some of the desiderata just described may seem incompatible with one another, especially if a single, simple device is envisioned, we think each has sufficient merit to warrant serious consideration. We would prefer not to attempt prioritization until more is known about the surface of Mars (from Viking, principally) and the actual constraints to be imposed on a sample return mission.

Ancillary scientific investigations should obviously be subordinated to the prime goal of obtaining and returning a sample of Mars surface material. Nevertheless, valuable science information may be lost without real-time, visual observation for selection of the sample and manipulation of the sampler. Imagery of the sampled environment could greatly enhance the scientific interpretation of the results of laboratory studies of the sample and could even prove essential to assuring that a collectable sample can be located, especially if hazardous obstacles posed a threat to the sampling device.

E. Landing Site: Conditions and Constraints

While it is obviously premature to make specific recommendations of areas or localities on Mars from which a sample should be obtained, certain general characteristics of sample sites can be recognized, and some of their consequences inferred. In general, the "younger," "volcanic" hemisphere of the planet differs from the "older," more

heavily cratered hemisphere in that its surface form and materials result more directly from Martian volcanic and weathering processes than from impact tectonics. Major areas of accumulation of transported material that may be natural samples of relatively large areas of the planet appear to be present in that hemisphere. The probability for finding fragments of unaltered volcanic material, from which we could learn something of the petrology of Martian volcanism, is greater there.

We recommend against sampling in areas of thick accumulations of aeolian deposits on the grounds that moderately coarse (2-4 mm and larger) fragments might be rare. Coarse fragments are optimum for many textural and other petrographic studies. Areas of bare rock might preclude successful landing or sampling. Even though they might provide a sampling of material derived from depth, samples from heavily cratered areas might be extensively contaminated by meteoritic matter.

A wide variety of materials is desired and might be collected at the locus of accumulation of transported debris, such as a canyon mouth. Landing in the vicinity of apparently young volcanoes would seem to favor the acquisition of fresh volcanic products.

F. Effects of Sterilization on Martian Minerals

Possible effects of sterilization by heating of Martian material can be separated into two categories: degradation and metamorphism. Degradation occurs when hydrous silicates and carbonates lose H_2O or CO_2 during heating. This effect is most pronounced for heating in vacuum, where volatiles are removed continuously. Hydrated silicates most susceptible to this type of degradation are clays and zeolites; those least susceptible are amphiboles and micas. These reactions will almost certainly be rate controlled because of the formation of anhydrous surface layers which slow the diffusion of additional H_2O through the surface. There is no quantitative information available in the literature on this type of degradation, and the temperatures quoted below for the onset of degradation are mostly guesses. This is an area where careful, well-conceived experiments are badly needed.

The effects of metamorphism are more difficult to assess and depend initially on the levels of PH_2O reached during sterilization. These levels will be highest if heating occurs in a sealed container and either water is added or a large amount of hydrous material is originally present in the sample. Heating under these conditions could produce water vapor pressures of as much as 100-200 atmospheres. Glasses containing water dehydrate and feldspars, pyroxenes, and olivines may begin to alter.

Perhaps the most delicate property to be affected by sterilization is the extent of oxidation. This problem is discussed in detail in the

letter by Sato (Appendix II). The two most likely effects are oxidation caused by loss of hydrogen and reduction caused by reaction with graphite or organic matter, if present. In that the fugacity of oxygen is a critical variable in both primary and secondary processes, the loss of such information can seriously degrade such information as temperature of formation, original mineral assemblages, composition of the atmosphere during weathering, extent of reduction of Fe to metallic form, and magnetic measurements. To overcome the loss of hydrogen, the sample should be sealed within a sample chamber lined with ultrahigh-purity gold.

Sterilization procedures will affect mineral species and their host rocks to varying degrees. Listed below are the approximate temperatures and general products of reaction for each mineral species for two assumed conditions of sterilization: (a) the original sample contains little water and the vapor pressure of water during sterilization does not build up to more than 1 atm. (Table 1a), and (b) the original sample gives off enough H_2O (or water is added before sterilization) so that the vapor pressure of water reaches values of 100-200 atm. (Table 1b). Table 2 contains a summary of the types of degradation that occur with increasing temperature. Most of the data of Tables 1 and 2 were derived from the letters from Hower, Fournier, Anderson, Papike, and Bence, Smith, Bailey, Frondel, Skinner, and Sato in Appendix II.

Table 1a. Water content small, vapor pressure <1 atmosphere.

Substance	Temperature	Effect
Feldspars	∿ 700°C	Structural changes, homogenization, incipient exsolution in quenched feldspars
Pyroxenes	∿ 700°C	Partial oxidation, homogenization, exsolution in quenched pyroxene
Olivines	∿ 500°C	Partial oxidation
Amphiboles	∿ 600°C	Dehydration and oxidation
Micas	∿ 500°C	Dehydration and oxidation
Glass	∿ 700°C	Devitrification
Iron oxides	∿ 250°C	Oxidation (or, possibly, reduction if graphite present)
Iron hydroxides	∿ 200°C	Dehydration and oxidation (or possibly reduction if graphite present)
Sulfides	∿ 200°C	Homogenization or exsolution and decomposition

Zeolites	< 200°C	Dehydration
Hydrated sulfates	< 100°C	Dehydration
Clay minerals	< 100°C	Dehydration and dehydroxyllation
Carbonates (Fe)	< 200°C	Decarbonation, oxidation
Carbonates (CaMg)	< 400°C	Decarbonation
Carbonates (NaK)	< 100°C	Decarbonation leaving highly reactive residuum
Halides	< 100°C	Hydrated -- anhydrous halides
Amorphous compounds		
Opaline silica	< 250°C	Recrystallization and dehydration
Limonite (see iron hydroxides)		
Ice	< 0°C	Melt

Table 1b. Water content large in sample, sufficient to build up a vapor pressure of up to 100-200 atms.

Substance	Temperature	Effect
Feldspars	∿ 300°C	Surface alteration to "micas"
Pyroxenes	∿ 300°C	Surface attention to chlorites
Olivines	∿ 300°C	Surface alteration to chlorites
Amphiboles	∿ 300°C	Partial alteration to chlorites
Micas	∿ 300°C	Hydromicas?
Volcanic glass	∿ 300°C	Devitrification + partial "alteration"
Iron oxides	∿ 250°C	Hydration and oxidation (or reduction if graphite present)
Iron hydroxides	∿ 200°C	Oxidation (or reduction)
Sulfides	∿ 200°C	Homogenization or, if quenched sulfides, exsolution
Zeolites	∿ 300°C	Partial dehydration
Clay minerals	∿ 150-200°C	Dehydration, dehydroxyllation
Carbonates (Fe)	∿ 200°C	Decarbonation, oxidation
Carbonates (MgCa)	∿ 400°C	Decarbonation, partial production of basic carbonates

Carbonates (NaK)	∿ 100°C	Decarbonation, reactive residuum, partial solution in vapor phase
Halides	∿ 100°C	Dehydration, partial solution in vapor phase
Amorphous		
Opal	∿ 150°C	Recrystallization
Ice	∿ 0°C	Melt

Table 2. Major types of information lost with increasing temperature of sterilization.

	Dry	Wet
100-150°C	Some hydrous "evaporite" phases dehydrated, largely recoverable information lost on clays. Interpretive loss not great.	Water-soluble efflorescences destroyed. Much information on possible soil brines, gas-rock interaction lost. Nitrate loss precludes information on N_2 in gaseous fraction of sample.
200-300°C	Clay structures irreversibly changed, limonite dehydrates to hematite, interpretative reconstruction can probably provide gross characterization of original material. Fine details of conditions of formation lost, but broad characterization of some conditions possible. Some auto oxidation with concomitant loss of redox information.	Clays preserved or only reversibly dehydrated. Primary silicates likely to hydrate and compromise petrogenic interpretation with very serious impact on alteration/weathering studies.
> 400°C	Ca-Mg carbonates decarbonate. Significant but not fatal loss of information regarding alterations and weathering processes.	
500+	Clays, zeolites, most hydrous alteration phases destroyed (limonite, etc.). Almost total loss of information on weathering, etc.	
700+	Primary minerals altered and petrogenic interpretation severely impacted.	

The above information in Tables 1 and 2 on carbonates is based on the assumption that the system remains closed. If open to vacuum, allowing the loss of CO_2, the carbonates will undergo decarbonation at temperatures between 150 and 200°C. A minimum vapor pressure of CO_2 of about 10 bars must be maintained if decarbonation reactions are to be inhibited.

If living systems have occurred on Mars in the geologic past, the preservation of their fossils relates to conditions, processes, and events required for the origin of living systems; the nature of the primitive Martian environment and its evolution with time; and the evolutionary flexibility and adaptability of biologic systems. It is known that certain irreversible changes take place in fossil remains as temperature increases. Chemical changes may occur at temperatures as low as 150°C and fossil textures may become somewhat altered at 300°C. These temperatures are largely based on educated guesses of Schopf (Appendix II) as few experimental data are available.

G. Effect of Sterilization on Fluid Inclusions

Study of the behavior of fluid inclusions in minerals during heating and refrigeration can yield uniquely valuable information concerning the physical and chemical conditions under which the mineral formed. No other technique gives such direct information on the composition and state of fluids present in the mineral-forming environment. Thermal treatment below 500°C will have relatively little effect on most observations, except for incompetent and cleavable minerals such as carbonates and nitrates, which are expected to decrepitate at significantly lower temperatures, perhaps as low as 150-200°C. (Appendix II, Roedder letter.) Sterilization heating at 150-200°C may, therefore, significantly reduce the information obtainable regarding the conditions of formation of some relatively low temperature minerals. Petrogenetic interpretation of "primary" rocks will not be greatly affected by heating to temperatures below 500°C.

H. Effect of Sterilization on Geothermometry

Mineralogic geothermometry uses data obtained from studies of phase equilibria on synthetic systems to determine the composition of a solid solution pair as a function of temperature and pressure. The upper and lower limits of stability of a mineral assemblage can also be determined as a function of temperature and pressure. For solid solution geothermometry, a temperature of formation is rarely determined in natural assemblages. More commonly, a temperature at which diffusion in the minerals ceased is determined, which gives information on cooling rate. Determinations on limits of stability are less precise since only an upper or lower limit of temperature and pressure of stability can be obtained.

Heat sterilization procedures will make any determinations of solid solution geothermometry invalid for assemblages whose temperatures of equilibration are less than about 100°C above the sterilization temperature. That estimate would be affected by the original cooling rate of the solid solution and the duration of sterilization.

Maximum temperatures of formation based on mineral stability will not be compromised if the assemblage does not decompose below the sterilization temperature, provided that the conditions of decomposition are not markedly affected by the nature of the vapor phase in equilibrium with the assemblage. The minerals most resistant to heat sterilization are those with low diffusivity; these are usually hard minerals with high melting points. Therefore, mineral assemblages in basalts and high grade metamorphic rocks are most likely to survive, provided that the vapor phase is not greatly different from that present during the history of the assemblage on Mars.

Determination of minimum temperature of formation is rarely obtained in unsterilized samples unless the cooling rate of the sample exceeds the decomposition rate. The same principle applies in heat sterilization procedures. If a metastable mineral assemblage decomposes during sterilization, then the minimum temperature of formation cannot be ascertained.

Those minerals most amenable to geothermometric methods are silicates, transition element oxides, sulfides with high melting points, and carbonates. Those that would not provide geothermometric information after sterilization are hydrated minerals, oxysalts, sulfides with low melting points, and most minerals formed as sublimates or efflorescences.

Once a sterilization procedure is decided upon, a list of minerals most suitable for geothermometric determinations could be drawn up, since most of the needed data on phase equilibria are available.

I. Effect of Sterilization on Gases Involved in Mineral Reactions

Volatiles such as CO_2 and H_2O are present on Mars. Their presence makes the Martian environment more akin to that of the Earth than that of the Moon. Not only may the primary minerals from igneous rocks contain hydrous silicates, such as amphiboles and micas, but surface processes, such as chemical weathering, must also be considered. The interaction of the primary minerals with fluids such as CO_2 and H_2O can, to some extent, be inferred from the mineral assemblages of the returned samples.

The oxygen fugacity for the equilibrium mineral assemblages can be determined by methods worked out by Sato for determination of the

"intrinsic oxygen fugacity" of a mineral. Such measurements would be extremely important to define the role of oxygen in Martian volcanic processes and the origin of the Martian atmosphere. However, as Sato and Wones point out in their letters (Appendix II), the preservation of the oxidation state of the returned sample depends critically on the sterilization procedure. Heating in vacuum entails loss of hydrogen and, hence, change in oxidation state. If graphite is present, heating may produce reduction of silicates and oxides by reaction with graphite.

Partial pressures of volatiles such as H_2O and CO_2 at the time of mineral formation can be estimated by simulation experiments on synthetic equivalents of the minerals contained in the returned samples.

J. Conclusions on Sterilization Procedures

We conclude that sterilization should be avoided. If required, it should be done at as low a temperature as possible ($\sim$ 200°C or less) with complete retention of any liberated gases. Time of sterilization, within reason, has much less effect on mineralogical properties than increased temperature. It is of paramount importance to measure and record the time-temperature-pressure conditions during any sterilization. Much information contained in the pristine sample might thus be recovered. A sealed liner of high-purity gold is required to overcome the loss of hydrogen and its associated effects on the redox conditions of the minerals.

No water or any other components should be added to the sample for the sterilization process. Although the presence of some water might help preserve some clay minerals and zeolites, these potential benefits do not begin to offset the disadvantages. If a large pressure were to develop in a sealed container because of heating for sterilization, a separate compartment might be designed to contain a water trap. Every effort should be made to recover all the gases released on return to Earth. However, the vapor pressure of CO_2 over the sample should not drop below 10 bars in order to avoid decarbonation reactions.

A thorough understanding of the reactions during weathering requires that the atmospheric composition be known. Furthermore, knowledge of the atmospheric composition would allow a more realistic evaluation of reactions occurring during sterilization versus those resulting from Martian weathering. For these reasons it is recommended that a separate sample of the Martian atmosphere be collected and returned.

K. Supporting Experiments

In addition to the detailed mineralogical and petrographic characterization of the returned samples, laboratory experiments will help extract

the maximum amount of information. Some of these experiments are simulations to be carried out prior to a sample return mission; others would be done on the Martian samples themselves.

1. Prereturn Experiments

   a. Information available on the thermal degradation of hydrous silicates and carbonates is based primarily on studies done at atmospheric conditions or at high gas pressures. Sterilization could involve heating to several hundred degrees in a near vacuum. It would be desirable to determine the effects of such heating on some of the more likely mineralogical candidates for the Martian sample. A beginning in this direction has been made by the "Preliminary Mars Sample Study" (Appendix III). Rather than to subject a large number of terrestrial grab samples to a variety of conditions, we recommend a few carefully designed, quantitative studies on clays, carbonates (including alkali carbonates), and carbonate-silicate mixtures. These studies treat in a sophisticated manner the kinetics and mechanisms of the decomposition reactions, so that our ability to predict effects of heating is enhanced and can be extended somewhat beyond the particular compounds studied.

   b. The second group of prereturn experiments is more difficult to specify, but equally important. It concerns the continual upgrading of laboratory capabilities between now and the time of sample return. To assure the maximum benefits from measurements on returned samples, good laboratories should be encouraged to take advantage of new technological developments and to maintain state-of-the-art capability in mineralogic and petrographic analysis.

2. Postreturn Experiments

   Postreturn experiments to be done on the returned samples (in addition to petrographic and mineralogical characterizations) include definition of temperature history of Martian minerals, estimation of gas pressures during Martian rock-forming processes, and attempts to reconstruct dehydrated or decarbonated minerals.

GEOCHEMISTRY

A. Introduction

The chemical composition of a terrestrial planet places strong constraints on its origin and evolution. This has been demonstrated by the major insights gained from geochemical studies on the returned lunar samples. It is clear from knowledge gained from the lunar studies and from the constraints of densities, moments of inertia, etc. that major geochemical differences exist among the inner planets. Accordingly, the chemical characterization of any returned Martian sample is essential. Refinements in analytical techniques, resulting in large part from lunar sample studies, have enabled these experiments to be carried out on small amounts of sample (often less than 50 mg.). Thus, very comprehensive studies of different materials present in the returned Martian sample can be obtained from a minimum amount of material. A somewhat more extensive discussion of the types of information about the origin and history of a planet that can be obtained by detailed chemical study is given below. For a really sophisticated understanding of the information to be gained from studying rather random samples collected without careful geological control and the extensive implications for the origin and history of the materials and their parent bodies that can be inferred from those studies, the reader is referred to the vast literature on chemical investigations of meteorites and lunar samples.

In considering the effects of the proposed biological sterilization on a returned Martian sample, we have separated the elements into different groups which would be affected to differing degrees by the sterilization procedure. We have also considered the state of the art for various analytical techniques and have made some evaluations and suggestions for improvement. The information on each experiment is organized in the following manner: (a) the elements to be analyzed are identified and current techniques for their analyses are evaluated; (b) the information to be gained on planetary evolution and history from the analysis is summarized; (c) the effects that biological sterilization might have upon the entity to be measured are estimated; and (d) suggestions for further development of analytical techniques or studies on the effects of sterilization are identified.

A number of gross simplifying assumptions were made in our evaluation of the effects of sterilization. Because of the disastrous consequences to chemical measurement, we assumed that no water or other substances would be added to the sample. Furthermore, we have ignored the effects of fluxing and etching that might result if hydrated materials and alkali carbonates were present in the sample and heated together in a closed container. Except in the sections where water

and carbon dioxide are discussed, or where explicitly stated, samples are presumed to be dry, and effects and temperatures refer to the dry material. Of course, the bulk composition of the original material can still be obtained no matter what chemical changes would result from a sterilization as long as the sample container remained sealed during heating. The potential loss of information on individual pieces of the sample could be severe, however, under any condition that would cause movement of volatile elements, diffusion, dissolution, or any other type of homogenization or redistribution of elements. The magnitude of this problem can readily be imagined by considering the effects of sterilization on mineralogy as discussed in the previous section of this report and realizing that a detailed chemical analysis of single grains or single minerals is an essential part of characterization of the sample.

B. Analysis for Water, Hydrogen, and Oxygen

1. Water

The simplest measurement of water content is the total mass of water that can be driven from the sample. These measurements can be done on very small sample ($\sim$ 5-10 mg) by a variety of standard techniques which may require some adaptations to this purpose. Such a measurement is very crude in the amount of information it provides about the sample and should at the very least be done in a differential thermal (DTA) mode. At the opposite extreme of sophistication is that undefined series of measurements that would demonstrate the location and the nature of the chemical bonding of all the water within the individual components that make up the samples. This series of measurements might include a variety of spectral studies combined with changes in spectral properties as a function of temperature during heating of the sample.

Information derived from water content of samples is related to the outgasing of the Martian planet and the extent and time of volcanic activity. It is also related to the processes and extent of weathering of igneous Martian materials to their present condition. Water may have played an extensive role in developing the observed morphology of the planet. The relationship between the water in the sample and the water content of the Martian atmosphere contains information on secular variations and Martian atmospheric composition. The observed water abundances will relate to the possibility for past and present Martian organisms.

Significant loss of water could begin at very low temperature and would be essentially complete at a temperature of at least 600°C (Gibson and Moore, Appendix III). In the case that the material at the Martian surface contains sufficient amounts of water that

are in equilibrium with ambient Martian surface conditions, significant water loss could occur with any decrease in partial pressure of water in the atmosphere of the sample container or with any increase in temperature of the sampled material. Water of hydration, which is less rapidly subjected to ambient surface conditions might, nevertheless, be lost during the long journey between Mars and Earth and in any event would be lost with increasing temperature -- especially up to 105°C. More strongly bonded water of hydration will be lost at yet higher temperatures and the extent of this loss may depend in a crucial way on the duration of heating during sterilization. The table by Nava (Appendix III) shows loss of water from most tested materials. Extent of weight loss as a function of time and temperature for the same materials is demonstrated by the work of Gibson and Moore (Appendix III). See Gibson and Johnson (1972) for further information of this type.

Because of the significance of the implications of the nature and quantity of water that may be found in Martian samples, experiment development for determination of the characteristics of water on very small samples should be supported. These techniques should then be used to study the characteristics and abundances of water in a wide variety of simulated Martian materials (see Appendix III). Such studies are a prerequisite for the understanding of the effects of sterilization on Martian samples.

2. Hydrogen

Total sample hydrogen and possibly some information relating to the chemical form of hydrogen in the sample can be obtained from gas release measurements (Gibson and Moore, 1972). Hydrogen is a major constituent of water. We note that very sensitive techniques have been developed for measuring concentrations of hydrogen as a function of depth beneath surfaces of rocks or mineral grains. Such techniques might prove useful where studies of diffusion rates of water into mineral surfaces were to be considered. Even weak sterilization of the sample is likely to degrade the diffusion gradient for hydrogen in the sample. Note also that hydrogen gas would escape from the container unless it were completely sealed and constructed of material (e.g., gold) that was impermeable to that substance. This would result in important changes in the redox state of the sample as well as in loss of the hydrogen itself.

3. Oxygen

Oxygen, the other major constituent of water, is normally determined by difference in geochemical silicate analysis. Corrections

can be made under some circumstances for the presence of significant quantities of other anions; e.g., sulfides or halides, or for metallic iron. It is possible to analyze directly for oxygen, for example, by fast neutron activation (Ehmann et al. 1972), but such a measurement is sensitive only to rather large deviations from normal stoichometry. Thus, little sample, if any, would be used for such a determination. Biological sterilization might result in the oxidation of indigeneous reduced species if the sample is not properly sealed and opened in a proper atmosphere.

C. Analyses for Carbon Dioxide and Other Forms of Inorganic Carbon

Like water, carbon dioxide may be either a major or minor constituent in a Martian sample. The simplest experiment to determine carbon dioxide is the measurement of total carbon dioxide lost from the sample on heating by commonly employed techniques applicable to small samples. The next level of sophistication is some form of DTA-evolved gas analysis (Gibson 1973). Considerable information is available for a variety of terrestrial and lunar samples using both heat and acid dissolution (Chang et al., 1974). Mineralogical characterization of carbonate minerals will be essential, and the nature of the bonding of carbon dioxide as an interstitial or adsorbed component should be determined (see Atmospheric Section -- Section 4). Spectroscopic studies can yield significant structural information on bonding of carbon dioxide constituents. The abundance of CO_2 in the Martian atmosphere is so large that its composition is expected to have played a significant role in the weathering of Martian materials. CO_2 may be a primary constituent of Martian igneous rocks. Terrestrial analogues of different occurrences of carbonates include igneous rocks such as carbonatites, sedimentary rocks such as limestone and dolomite which are produced by a combination of biological and chemical processes. Carbonate rocks formed by igneous and sedimentary rocks have different trace chemical characteristics from which the nature of their origin can be deduced (refer to Petrology Section). The relatively high proportion of carbon dioxide and low abundances of O_2 and H_2O in the Martian atmosphere may lead to a rich variety of carbonate and bicarbonate rocks that would be unknown at the Earth's surface. Correlations of carbon dioxide abundances with water and rare gases provide constraints on models of the outgasing history of the planet. The polar caps appear to consist largely of carbon dioxide and, thus, there is the possibility of sampling a permafrost of dry ice and related compounds. We note also that some carbon dioxide is a possible constituent in some vugs or fluid inclusions.

In addition to clearly present carbon dioxide, there will undoubtedly be small amounts of carbon present in other oxidation states.

It is noted that the suboxide of carbon, C_3O_2, an interesting compound of complex behavior, is solid below -111°C and melts at 7°C. The discovery of C_3O_2 or its readily formed polymer in a returned Martian sample would bear on the origin of certain observed Martian phenomena (Perl, 1971) or on the conditions of the treatment of the sample during its journey between Mars and Earth. Numerous other forms of carbon may be present. Their presence should provide useful information on processes that affect inorganic carbon in the Martian geochemical cycle. Extensive studies of carbon at the trace levels will be made by organic- and biochemists; we shall not further discuss the element carbon here. We note, however, that a total carbon analysis on a small sample is an important value that provides a knowledge of the general level of concentration of a cosmically important element in the sample and which serves as a constraint on the mass balances for carbon from other experiments.

The effects of sterilization on the carbon dioxide content will be roughly analogous to those on water. Degradation of the information available from analysis of carbon dioxide in the sample may begin during the return to Earth, especially if the sample container is not properly sealed.

Very special sampling would be required to obtain and maintain a sample that had frozen carbon dioxide liquid or gas with attendant high pressure. Adsorbed carbon dioxide or other loosely bound carbon dioxide will certainly be lost as the partial pressure above the sample is decreased or the temperature of the sample is raised. Carbon dioxide is lost from limestone in a relatively short time when heated at 400°C (Wendlandt, 1964). Heating at lower temperatures will result in a slower but measurable loss. Bicarbonates decompose at lower temperatures than carbonates.

Careful development of sophisticated techniques for the study of abundances and distributions of carbon dioxide in small samples in a wide variety of Martian analogues is needed. Such studies would enhance understanding of the effects of sterilization on these materials.

D. Analysis for Nitrogen

An upper limit of 5% nitrogen in the Martian atmosphere has been established (Dalgarno and McElroy, 1970; Owen, Appendix III). This raises the interesting question of whether significant quantities of nitrogen are present in the condensed surface materials. If present, nitrogen could be in the reduced form of ammonium ion, or more oxidized form of nitrate ion, or possibly as nitrite. Any disequilibrium between nitrogen in the returned sample and that in the Martian atmosphere could indicate important secular trends in the composition of the Martian atmosphere. The oxidation state of

nitrogen in the condensed material of the Martian surface is indicative of the redox conditions under which those materials formed. Note also the possibility of fixation of nitrogen gas into reactive nitrogen species by the action of biological organisms.

The presence of nitrogen-containing silicates such as ammonium feldspar, $NH_4AlSi_3O_8$, is a possible constituent in the Martian surface samples. Ammonium silicates are stable at partial pressures of ammonia between 1 and 10^{-4} bar, and can release ammonia during progressive metamorphism (temperatures between 500-700°C) by thermal decomposition, dehydration, or cation exchange. Ammonium ion could be a significant constituent of Martian rocks that, on oxidation during metamorphic processes, might provide nitrogen gas to the Martian atmosphere. Inorganic materials such as NH_4HCO_3, $(NH_4)_2CO_3 \cdot H_2O$, NH_4NO_3, and NH_4Cl, all potential Martian surface materials all of which begin decomposing between 50° and 175°C.

Although numerous standard chemical methods can be used to identify and quantitate these forms of nitrogen, none has been satisfactorily adapted to the geochemical analysis for that element in very small samples of such precious samples as returned Martian samples.

Development of proper analytical methods for analysis of molecular forms of nitrogen at low concentrations in small samples is an important experiment. Unless such procedures are developed and applied to appropriate simulants, it may be difficult to assess the effects of biological sterilization on compounds of nitrogen in the Martian sample.

E. Atmospheric Composition

The composition of the Martian atmosphere has been reviewed by Owen (1974), who has provided the following table.

Composition of the Martian Atmosphere

Gas	Abundance (cm am)	Relative Abundance
CO_2	7500 ± 1000	$\geq$ 900,000 ppm
CO	13 ± 8	1,600
O_2	9 ± 2	1,100
H_2O*	2.5 ± 1.5	300
O_3*	2.5 ± 1.5 x 10^{-4}	0.03

*These constituents are known to vary with seasonal and diurnal cycles.

The analysis of the condensed portion of the returned Martian sample for the elements comprising the gases in the table has been considered above. Analysis of the exact composition of the atmosphere is a separate and very important measurement. The obvious method for making such a determination is mass spectrometry (or GC-MS). Analyses for noble gases and for isotopic ratios for all constituents are considered in the next section of this report. This section is concerned only with the molecular concentrations of the various species that are present in the atmosphere except for the noble gases.

Measurement of the actual atmospheric composition from a returned sample may prove impossible because the dynamic chemical equilibrium among the atmospheric gases may be disturbed by the sampling process. At the very least, an atmospheric sample separate from condensed material would be required, because the equilibrium between the condensed material and the atmosphere can be readily disturbed as the temperature or total pressure on the combined sample was changed. Such a disturbance might be severe for the atmosphere but negligible for the condensed phase because of much larger quantities of the elemental constituents of the atmosphere in the condensed material. Methods of obtaining an isolated sample of the atmosphere might include simple filling of an evacuated inertbomb, an attempt to condense an atmospheric sample to the cold temperatures of space, trapping of a sample on an appropriate molecular sieve, or adsorption on an activated surface. It is highly probable that any of these techniques would seriously disturb the equilibrium concentrations of the constituents and could cause such constituents as ozone to disappear altogether. Thus, extensive experiments are required merely to determine the accuracy with which an atmospheric sample collected by any technique could be used to infer the composition of the atmosphere originally sampled. Certainly, biological sterilization at any temperature would seriously disturb the molecular balance of the sample. The most satisfactory determination of the composition of the Martian atmosphere in the sense of the equilibrium molecular concentration would probably be one done in situ. A separate sample of the Martian atmosphere would, at the very least, provide the important constraint of knowing the bulk elemental composition of the atmosphere.

Whether or not a serious attempt is made to provide a separate sample of the Martian atmosphere, any gases collected with the sample of condensed phase surface material should be retained, as should any gases released from the condensed material as a result of sampling and transport to Earth, even if biological sterilization is done. It is important to know to the best available approximation the extent to which the condensed material may have outgased adsorbed atmospheric molecules, or reacted with the atmosphere. This can only be done if the gases included in the container with the returned Martian sample are carefully analyzed. The materials of the sample

container must not add gas to or subtract gas from the sample by outgasing or by reactions with the gaseous materials accompanying the sample.

In light of the above discussion, it would appear that, in the event of a trade-off in weight, more is to be gained by returning additional condensed surface material than would be obtained from a separate atmospheric sample.

F. Analysis for Major Elements

The major elements are Si, Al, Ti, Fe, Mg, Ca, Na, K, and P. The major elements comprise the bulk constituents of the terrestrial planets and meteorites. Major element analysis furnishes the basic set of compositional data for the bulk material that is essential to the execution and interpretation of a high portion of all other experiments done on Martian material. Major element data also furnish an index of the extent of differentiation of the Martian materials analyzed from parent matter of more primitive composition, including differentiation during accretion of the planet with respect to primordial solar system matter as well as differentiation within the planet accompanying its evolution as a planet. It should be noted that phosphorus is an organogenic element and plays an essential role in terrestrial biology.

The well-established technique of wet chemical analysis is not recommended for Martian materials because of the relatively large sample size ($\gtrsim$ 1 gm) required to generate data of competitive accuracy (e.g., Jarosewich, 1967). At the present time, X-ray fluorescence is the favored method for major element analysis on such materials. No more than 300 mg of sample are required for an accurate analysis, including the amounts needed for supplementary analysis of the alkali elements by atomic absorption (Norrish and Hutton, 1969: Rhodes and Hubbard, 1973). Major element analysis of somewhat lower precision can be obtained by atomic absorption spectrophotometry on samples weighing as little as 10 mg. This makes analyses of very small subsamples of the main sample possible. Instrumental neutron activation analysis for sodium and manganese should be done before the sample is dissolved for the atomic absorption experiment (Nava and Philpotts, 1973; Helmke et al., 1972). Instrumental neutron activation analysis for most major elements can be done on samples ranging downward in size to 1 mg (Laul and Schmitt, 1973). The precision of these analyses is somewhat less for most elements than that obtainable by the previously mentioned techniques. Methods of bulk analysis for major elements by electron probe measurements on samples as small as 1 mg are now being developed and should be competitive in precision for most major elements by the time the Martian sample is returned (Reed and Ware, 1973). Some major

elements can be analyzed in very small samples (∿ 1 mg) by mass spectrometric isotopic dilution with excellent precision (Hubbard et al., 1973).

Loss of H_2O, CO_2, NH_3, or similar gaseous, light-element constituents might result in a significant change in sample weight. Thus, the material analyzed may give a somewhat modified characterization of the bulk composition of the surface material. (Refer to sections on H_2O, CO_2, and N_2 for further discussion.) Such an effect would be observed or deduced in part from petrological and mineralogical examination of the sample. The extent of this change, if severe, cannot be definitely determined from analysis of the sample after it has been heated. Nevertheless, very useful information pertinent to the extent of differentiation of the planet from primordial material and from its initial conditions is retained in the ratios of concentration of the less volatile components. Thus, additional information on the nature of the original material prior to loss of water and carbon dioxide can be inferred.

As pointed out in the sections on H_2O, CO_2, and N_2 there may be significant weight loss over the range of temperatures from that of the sample at the time of its collection up through a few hundred degrees centigrade. Near the upper end of this range (400-700°C) the weight loss may be further aggrevated by the thermal decomposition of sulfides (400-500°C), if present, and K (850°C), Na (1050°C), and SiO_2 (> 1000°C) will distill away from the more refractory portions of the sample (Gibson and Hubbard, 1972). The analyses for any elements distilled away would be disturbed over and above the effect from the weight loss of the sample. Possibilities for K-Ar or ^{40}Ar-^{39}Ar age measurements become very poor (see the next section).

In interpreting his experimental results on major elements in heated simulants, Nava (Appendix III) found, even at low temperatures, effects on the concentration of sodium in the samples that could not be simply accounted for by weight loss. Much additional information on conditions of loss of major elements by heating on a wide variety of materials can readily be obtained from the literature of experimental petrology. No further work on this problem is probably needed unless sterilization at temperatures above 400°C for at least several hours are seriously considered.

G. Analysis for Sulfur

In major element analysis by X-ray fluorescence, the element sulfur is frequently determined (Norrish and Hutton, 1969). Total sulfur can also be accurately determined by use of a sulfur analyzer (Gibson and Moore, 1973). Both of these analyses can be done on relatively small samples (100-200 mg). Not only the total sulfur abundance but

also the chemical forms of sulfur are of interest. Oxidation states for sulfur ranging from sulfides to sulfates must be anticipated in Martian samples. Some information about chemical forms of sulfur can be obtained by thermal gas release experiments, again on small samples (25-50 mg, Simoneit et al., 1973). Petrographic analysis can establish the occurrence of sulfide and sulfate minerals.

Sulfur and its compounds are common products of volcanic emissions. The concentrations and forms of sulfur in Martian samples thus will serve as indicators of the extent and nature of past Martian volcanic activity. On a geological time scale, sulfur from volcanic emissions reacts with the constituents of the atmosphere and becomes involved in the sedimentary cycle on Earth. With due respect to differences in compositions, analogous reactions are expected for Mars and could well result in a variety of compounds (minerals) not found on Earth. Sulfur dioxide may be important in processes of Martian weathering. The geochemical cycle of sulfur on Earth is influenced by biological activity and a similar influence cannot now be ruled out for Mars. Furthermore, it is important to determine the origins of any sulfur minerals on Mars. A meteoritic contribution of troilite is anticipated. The combined effects of impact and weathering in the Martian environment may make it difficult to detect the meteoritic component, except by detailed trace element studies.

Serious degradation of information on sulfur is expected to result from sterilization procedures even at low temperatures. Loss of information regarding the oxidation state of sulfur would accompany any decomposition of sulfur phases. Sulfate decomposition begins at about 300°C. Loss of sulfide sulfur is extensive over the range 200-700°C, depending on the compound. If the sample is heated to temperatures above 300°C for more than a few hours, the only remaining information on sulfur in the sample may be the total sulfur content, and that only if the container is properly sealed. Sulfur compounds can be oxidized or reduced by gases released by the sample or in the atmosphere as soon as any temperature change above ambient Martian conditions occurs. Such degradation could be extensive during the long transit from Mars to Earth. In particular, at reduced pressures, elemental sulfur sublimes readily across any temperature gradient. Furthermore, any adsorbed gases such as H_2S and SO_2 will be lost if the temperature of the sample is raised above ambient Martian levels.

Further development may be needed on analytical techniques for determining the oxidation states and the chemical bonding in small amounts of Martian simulants. Studies are badly needed to determine the effects of sterilization procedures on the abundance, oxidation state, and distribution of sulfur containing compounds and minerals in such materials. Effects on some sulfur minerals have been discussed in the previous section of this report.

Care must be exercised in the choice of material for the returned sample container because sulfur and its gaseous compounds can react with over-long time periods with many materials.

H. Analysis for Chalcophile Elements

Some examples of geochemically important chalcophile element group are: lead, copper, thallium, bismuth, and mercury. All except lead are now commonly studied by neutron activiation analysis; lead is usually determined mass spectrometrically by isotope dilution techniques (e.g., Morgan et al., 1973; Jovanovic and Reed, 1973; Silver, 1972; Nunes et al., 1973; Tera and Wasserburg, 1972). The state-of-the-art for these measurements is generally satisfactory for work on small samples; however, little information can be inferred about the chemical forms by these techniques. In lunar studies, these elements are sensitive indicators of the extent of differentiation of that body from primordial solar matter and, therefore, of the accretionary history of the Moon. Because of their relatively volatile nature, these elements are mobilized at the lunar surface, presumably by impact heating. They can be used as an index of fumarolic activity. Since these elements are enriched in carbonaceous chondrites, they also serve as indicators of the contribution of primitive meteoritic or cometary material to the surface of Mars. Because the meteoritic influx to Mars may be greater than that in the vicinity of the Moon, a possible larger input of meteoritic material to Mars is anticipated (W. D. Metz, 1974). On Earth, some of these elements are concentrated in ore deposits resulting from igneous or hydrothermal activity. Similar concentrations on the Martian surface would indicate a type of chemical differentiation on Mars similar to that found on Earth but lacking in the Moon.

Because of their relatively volatile natures, the distributions of these elements in Martian samples can be seriously disturbed by sterilization. Mercury volatilizes readily at low pressures at room temperatures and many of its compounds begin to decompose below 100°C. Loss of thallium and lead by volatilization is already rapid at 400°C which would have serious consequences for abundance determinations and for lead age measurements. Note that whenever such an element vaporizes it is not merely lost from the materials that initially contained it, but it contaminates the rest of the sample.

The range of materials studied and the range of sterilization conditions need to be extended for abundance and isotopic measurements beyond those performed by Nunes et al. (1973). Similar studies are required to document the behavior of other chalcophile elements during similated sterilization procedures. Additional experiments on sulfur and chalcophile elements should be considered to determine

whether the anticipated conditions of transport of sample from Mars to Earth will affect the geochemical information available from these elements. The value of geochemical information available from chalcophile elements warrants high priority for their further study.

I. Analysis for Siderophile Elements

Representative siderophile elements include nickel, cobalt, osmium, iridium, phosphorus, gold, and silver. These elements are now determined in geochemical analysis by neutron activation analysis involving chemical separations. Only small quantities of sample are required (20 mg), and the existing techniques provide adequate sensitivity (Morgan et al., 1973; Anders et al., 1973). Some improvement in the precision of the technique would be desirable for the platinum group elements, but will be difficult to obtain by mere refinement of existing techniques.

Indigenous Martian abundances of these elements provide essential information regarding accretion and differentiation processes and possible core formation. The concentrations of these elements in surficial Martian material would also provide an estimate of the amount of meteoritic infall. Fine subdivision of the classes of meteorites has been made using relative abundances of siderophile elements. Thus, information about both ancient and recent meteorite collisions with Mars and possibly, relationships of those meteorites to the nearby asteroid belt may be obtained.

In elemental form, the siderophile elements are generally refractory. Some of their simple inorganic compounds, however, decompose at temperatures as low as 200°C. Under highly oxidizing conditions, volatile osmium tetroxide can form. Therefore, significant information about the abundances of some of the elements might well be lost during biological sterilization. Important ratios such as Ir/Au could be perturbed by heating as high as 800°C even under reducing conditions.

J. Analysis for Refractory Lithophile Elements

The group of refractory lithophile elements includes barium, strontium, the rare earth elements, the heat-producing elements uranium and thorium, zirconium, hafnium, niobium, and others. At present, many of these elements can be measured on very small samples (10 mg or less) by mass spectrometric isotope dilution techniques, by neutron activation with and without chemical separation, and by spark source mass spectrometry (e.g., Hubbard et al., 1973; Nunes et al., 1973; Laul and Schmitt, 1973; Haskin et al., 1973; Taylor et al., 1973). These techniques achieve adequate precision and accuracy and provide important multi-element analytical capability for single samples.

The abundances of these refractory elements relative to more volatile elements (e.g., U/K, La/K, Zr/Cs) provide information on the temperature of condensation of the planetary constituents and on internal fractionation processes. These ratios are widely different in the Earth, Moon, and meteorites and provide chemical indices with which to distinguish the different condensation histories of bodies in various parts of the solar system. An example is shown in the figure below, taken from Eldridge et al. (1973). Detailed abundance patterns of the rare-earth elements can, for example, provide critical information on the melting and crystallization histories of volcanic rocks and on the composition of the interior of Mars. The extreme concentration of barium in the near surface region of the Earth and Moon, relative to the average concentrations inferred for the whole bodies, makes it an index of global differentiation processes. Strontium isotopic abundances are discussed in the next section on isotopes.

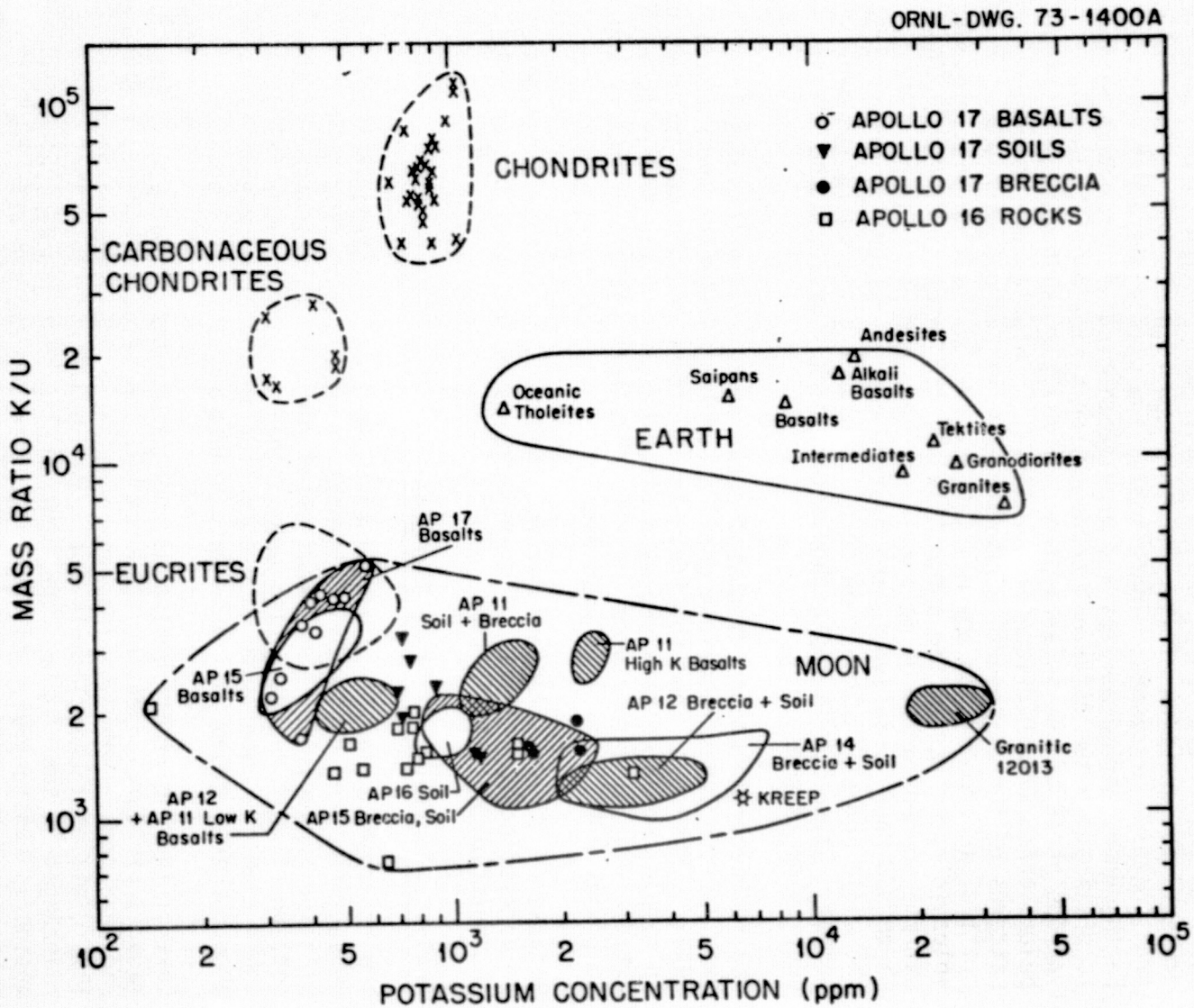
The refractory elements discussed above do not begin to volatilize from various lunar materials until above 1400°C (Gibson and Hubbard, 1972). This means that considerable important geochemical information in samples would be retained even after heating of the sample to extremely high temperatures, and insights into planetary history and composition will still be possible.

Because of their refractory nature, the need for further experiments to understand the effects of sterilization on their measurement is not anticipated at this time.

K. Analysis for Volatile Trace Elements

The chalcophile and trace alkali elements are considered in this subsection. The chalcophile elements have been discussed in a previous subsection. The alkali metal rubidium is discussed in the section of this report on isotopes. The reason for summarizing these elements here is to draw attention to their importance as a geochemical group in the sense of their volatile natures.

Loss of these elements begins at room temperature with mercury (at reduced pressure), leading at about 400° to relatively rapid thallium and lead loss. Rubidium loss commences at 700°C at temperatures of 1000°C all of these elements will have been seriously depleted or rearranged in the sample. The resulting loss of geochemical information is substantial. All age dating techniques are affected, evidence of the condensation history of the planet is seriously degraded, and insights into processes of Martian crustal differentiation and production of igneous rocks would be limited. Information on the influx and nature of meteoritic or cometary material will be lost.


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APOLLO 17 BASALTS
APOLLO 17 SOILS
APOLLO 17 BRECCIA
APOLLO 16 ROCKS
CHONDRITES
CARBONACEOUS CHONDRITES
EARTH
Andesites
Alkali Basalts
Saipans
Basalts
Oceanic Tholeites
Tektites
Granodiorites
Intermediates
Granites
MOON
EUCRITES
AP 17 Basalts
AP 11 Soil + Breccia
AP 11 High K Basalts
AP 15 Basalts
AP 12 Breccia + Soil
AP 14 Breccia + Soil
Granitic 12013
AP 16 Soil
KREEP
AP 15 Breccia, Soil
AP 12 + AP 11 Low K Basalts
MASS RATIO K/U
POTASSIUM CONCENTRATION (ppm)
10^5
5
2
10^4
5
2
10^3
10^2
2
5
10^3
2
5
10^4
2
5
10^5

L. Analysis for Ferromagnesian Elements

The ferromagnesian elements are those trace elements that enter into sixfold coordination sites in rock-forming minerals and include, for example, cobalt, nickel, iron, chromium, and vanadium. X-ray fluorescence and neutron activation techniques are presently used for measuring these elements (e.g., Haskin et al., 1973). Because of the much smaller sample size (10 mg) required by the latter method, it is preferred. However, further attention should be given to the development of more precise and accurate means of determining these elements in small samples. The distribution of these elements among mineral phases provides information on the crystallization histories of volcanic rocks and permits inferences to be made about the composition of the interior of the planet. These are the elements that are lost to solid ferromagnesian minerals during early crystallization of a silicate liquid or are retained in refractory ferromagnesian residues during partial melting. In the geochemical context discussed here (igneous rock-forming minerals), the effect of heating to 1000°C in the absence of water is not expected to alter appreciably the abundances and distributions of these elements. In the presence of water, however, alteration may occur at lower temperatures (see Petrology Section). No need for further study of the effects of sterilization on the measurement of these elements is anticipated at this time.

M. Analysis for Halogens

Halogens are presently determined by activation analysis involving chemical separation techniques. The required sample sizes are small (100 mg); however, improvements in sensitivity, precision, and accuracy would increase the value of the technique for analysis of Martian samples.

Volcanic emissions are the primary source of halogens at the surface of the Earth. By analogy, the presence and abundance of halogens in Mars surface samples would provide information on the nature and extent of Martian volcanic activity. The dissolution of metal halide salts in aqueous media provides a ready means of transport followed by deposition as evaporites on Earth. Determination of halogens in Martian samples could thus provide information regarding previous aqueous regimes. Substantial elemental losses through volatilization will perturb halogen abundance measurements at 150°C (Reed, Appendix II) in a dry material. Because of the mobility of halogens at temperatures above 100°C and their chemical reactivity, attention must be directed to appropriate choice of sample container material and method of sealing. If the sample contained appreciable water, production of an aqueous fluid on heating would destroy soluble halide minerals. Further experiments would be useful to determine the

effects of various sterilization regimes on the abundances and distribution of halogens in Martian simulants. In addition, the effects of halogens volatilized from Martian simulants on various container materials needs to be determined.

N. Redox Potential

Intrinsic oxygen fugacity measurements on mineral separates or rocks are made with the aid of an oxygen probe according to standard procedures (Sato, 1971). This direct method is preferred over measurement of Fe^{+2}/Fe^{+3} ratios. The oxygen probe method at present requires about 100 mg of material. Petrographic information provides extensive information on oxidation states (see previous section). Various spectral and spin resonance techniques and Mössbauer spectrometry also provide information on oxidation states for some elements (e.g., Morris and Haskin, 1974; Niebuhr et al., 1973; Burns et al., 1973). Measurement of the oxidation state of Martian rocks would provide valuable insight to the mechanisms which control the oxidation states of igneous rocks during their formation.

The effects of sterilization on the measurement of oxygen fugacity are discussed in the section on petrology. Improvements in and additional experiments on geochemical materials with all of the above techniques are needed to extend their general use as geochemical tools as well as their range of applicability to smaller sample sizes (less than 100 mg) than is possible at this time. Additional recommendations pertinent to the measurement of oxygen fugacities of Martian rocks can be found in the Petrology Section.

O. Surface Properties and Gas Interaction Studies

Among the interesting mechanisms operating on the Martian surface is the interaction and adsorption of atmospheric species with surfaces of materials in the soil. Information derived from gas interaction studies should relate to volatile transport processes operating on the surface of Mars. Grain surfaces may contain condensed elements volatilized from meteorite impact and Martian volcanism. Studies of grain surfaces will assist in identifying weathering processes. This atmosphere-soil interaction is one of the major ways in which Mars is expected to be unique, differing from the Earth, Moon and Venus. In this context a core sample might provide valuable information.

All of the information about gas interactions may be irreversibly lost at very low temperature (i.e., <100°C) during sterilization of the sample because such heating may seriously alter the properties of the surfaces of the grains and their ability to adsorb molecules.

If the sample does get sterilized, once its chemical and mineral compositions are known, experiments can be done on simulants as well as on portions of the Martian material to attempt to determine the original nature of the grain surfaces. Adsorption-desorption studies, SEM, and ESCA will be useful tools for such investigations.

P. Recommendations for Development of Analytical Methods Before Sample Return

In the previous sections we have identified a number of areas of experimentation which either require or would benefit from development of better analytical techniques. We have also identified some of the main gaps in knowledge that would allow a more accurate estimate of the effects of sterilization on the returned sample. It is not sensible to try to carry out all of the work suggested at this point in time. Decisions on the necessity for biological sterilization have not yet been made, nor the exact mode of sterilization, if sterilization is finally deemed necessary, defined. Information on the nature of Martian surface materials is meagre, at best, and should improve as a result of the forthcoming Viking missions.

Our first recommendation is that those laboratories that are presently doing high qulaity geochemical analysis in all areas discussed in this section be kept strong and busy. Studies of terrestrial, lunar, and meteoritic work must be continued, and at a level that enables the state-of-the-art to be improved. The Martian sample must be approached with the very best analytical program that can be developed. In addition to maintaining and improving the present strengths, we recommend development of micro techniques for studying water, carbon dioxide, and nitrogen and sulfur compounds. These techniques must not merely provide accurate elemental abundances on small samples, but must provide information on oxidation states compounds, and nature in techniques for analysis of halogens and noble (platinum-palladium group) metals should also be begun at this time.

Only a modest program of evaluation of effects of biological sterilization should be done at this time. The emphasis should be on behavior of water, carbonates and bicarbonates, and compounds of sulfur and nitrogen. Results from these studies, as well as those results given already, should be considered when a final decision on sterilization is made. If a decision to sterilize the sample is made, the protocols should be designed to provide minimal disturbance to the sample. Once protocols are established (if sterilization becomes a necessity), further studies of effects of sterilization on the potential returned sample can be designed. A more comprehensive program for studies can finally be designed when analytical results from the Viking missions become available.

Q. Summary of the Potential Effects of Heat Sterilization on the Inorganic Chemical Properties of a Returned Martian Sample

Any sterilization procedure (e.g., 150°C for 30 days) will affect to some degree the analytical information that could be obtained from the sample. In particular, information on water, carbon dioxide, compounds of sulfur and nitrogen, trace atmospheric gases (chemically active), halogens, oxidation states, gas adsorption properties and surface physical properties of the sample will be degraded. By raising the temperature to 250°C for 1 week, some important geochemical information on the chalcophile elements, especially Hg, will be lost. Raising the temperature to 350°C would virtually destroy almost all information on the chalcophile elements (Pb, Tl, S). The next serious element loss begins above 700°C where elements such as Rb, carrying with it vital information regarding age, begin to be lost from the sample. The only useful geochemical information retained above 1000°C is the abundance ratios of the refractory elements. See the accompanying table for more details.

All of the changes described above will begin at much lower temperatures in the presence of water, even water indigenous to the sample. Addition of foreign material; e.g., H_2O, ethylene oxide, abraded material from the sample container, etc., to the returned Martian sample will seriously compromise the scientific value of the sample. The interior of the sample container should be made of a single, high-purity element whose presence will not seriously affect the geochemical studies. Possible candidate elements are aluminum, tantalum, or gold, or oxides such as alumina or fused silica. Stainless steel would cause difficulties because of its multi-element composition. Most ceramic materials are unacceptable because of their high Rb content, which pose a serious risk to the Rb-Sr age technique. An material used to seal the container must be in the highest possible state of purity. Otherwise, serious degradation of information on volatile and chalcophile elements (e.g., Ag, In, Pb, Hg) could occur.

It is beyond the scope of this effort to select the most suitable material from which the sample container, which must be sealed to contain, possibly, a high pressure, should be made. The final choice must be a carefully considered compromise between scientific requirements and engineering realities.

Sterilization Effects upon Chemical Composition

Temperatures	150°C 30 days	250°C 1 week	350°C 1 day	500°C	700°C	1000°C	1500°C
Analysis							
Water, hydrogen and oxygen	XX	XX	XX	XX	XX	XX	XX
Carbon dioxide and inorganic carbon	X	XX	XX	XX	XX	XX	XX
Nitrogen	X	X	XX	XX	XX	XX	XX
Atmospheric gases	OK	OK	OK	OK-?	OK-?	X	X
Major elements	OK	OK	OK	OK	OK	?	XX
Sulfur and Chalcophile elements	?	?	X	XX	XX	XX	XX
Siderophile elements	OK	OK	OK	OK	OK-?	X	XX
Refractory elements-rare earths	OK	OK	OK	OK	OK	OK	?
Ferromagnesian elements	OK	OK	OK	OK	OK	?	?
Volatile elements	OK	OK	?	X	X	XX	XX
Halogens	X	X	XX	XX	XX	XX	XX
Redox Measurements	X	X	X	XX	XX	XX	XX
Gas-solid interactions	X	X	XX	XX	XX	XX	XX

OK= Not effected by sterilization
? = Sterilization effects not known
X = Slight damage produced by sterilization
XX = Major damage resulting from sterilization

Sterilization procedures considered are only for dry heat sterilization in sealed sample container and assuming insufficient indigenous water to dissolve or rearrange compounds and elements.

ISOTOPIC MEASUREMENTS AND AGE DETERMINATIONS

This section considers the importance of measuring the isotopic composition of certain elements in a returned Martian sample. Detailed consideration was given to the following broad areas: (a) variations in the isotopic compositions of the light elements hydrogen, carbon, oxygen, silicon, and sulfur; (b) the standard radiometric age dating methods of K-Ar, Rb-Sr, and U-Th-Pb; (c) information to be obtained in the study of rare gases in the Martian atmosphere and in solid samples; and (d) information to be gathered from the concentrations of radioactive and stable cosmic ray-produced nuclides in the Martian atmosphere and soil. In this introduction we anticipate certain conclusions derived in the following sections and summarize here the priorities which we place on certain investigations and the sampling necessary to maximize the information obtained therefrom.

Very high and approximately equal priorities are given to study of the stable iostopes of hydrogen, carbon, and oxygen and to the determination of radiometric ages.

Isotopic dating and stable isotope measurements are most profitably applied to lithic fragments. The study of such samples defines specific events and conditions of igneous and metamorphic activity, sedimentation, and hydrothermal alteration on Mars. Constraints are provided on the thermal history of Mars, including formation, crustal differentiation, and the cataclysmic bombardment evidenced by the heavily cratered surface, as well as the history of volatiles and of the hydrologic cycle. The greater the number and variety of individual lithic fragments, the more extensively this history of Mars can be delineated, and the stronger the constraints become on inferences about past and present physical conditions.

Results obtained on soils are useful but, in general, will be more ambiguous than results obtained on coherent rock fragments. They provide average measurements (age and mean isotopic composition) over the wider region contributing to the soil grain population, thus characterizing the local, or possibly even global, Mars surface. Age statements are generally limited to model age calculations, which give indications of age only under certain assumptions. Results are made more specific by analyzing separated fractions with shared characteristics or by recognizing that some measurements are dominated by a particular mineral or mineral assemblage. Comparison of results from a lithic fragment with those from a soil measures the characteristics of the fragment against the average character of a much wider region. The soil contains information about the Martian surface mixing and volatile and grain transport processes.

The sampling technique should be designed to provide a sufficient number of fragments up to a centimeter in size in order to provide a sufficient quantity of material in a single fragment for mineral separation. The sampling technique should include representative soil material.

High priority is also placed upon measurement of the isotopic properties of a sample of Martian atmosphere. This will not only yield information about atmospheric processes and degassing of the planet but will also yield baseline information for interpretation of the isotopic composition of certain elements present in the solid samples. To this end, a separate sample container (or portion of the main sample container) should be considered. If any kind of heat-treatment sterilization is applied to the container, the atmospheric sample must be kept separate from the solid sample. The sampling procedure cannot utilize any kind of adsorption technique, inasmuch as isotopic fractionations will occur during such a process. The best type of sampling device would be to simply open a 500-1000 cm^3 container, let it equilibrate at ambient temperatures on the Martian surface, and then seal it prior to liftoff.

Somewhat lower priority is placed on the measurement of cosmic ray-produced nuclides. These measurements are not apt to yield fundamental information concerning the formation and evolution of the planet as a whole. However, they will almost certainly yield important information concerning relatively recent surface processes, and the interaction between surface and atmospheric processes.

A. Stable Isotopes

A summary of the conclusions of this subsection is given in the accompanying table. Following are more detailed statements.

1. Oxygen

Oxygen isotope analyses of coexisting minerals from a returned Mars sample should prove very useful in the following ways: (a) estimating the temperatures of formation of the mineral assemblages in any returned rock fragments, and (b) in determining whether or not the minerals in such rocks or in the bulk soil were formed in equilibrium, or whether they represent different stages of mineral formation. Certain minerals are inherently much more susceptible to ^{18}O-exchange than are others, and analyses of these may allow us to monitor secondary alteration processes that have affected the rocks or the soil (such as exchange with H_2O, CO_2, etc.). This type of isotopic study is essential in interpreting the origin and history of H_2O and CO_2 in the rocks and the atmosphere of Mars.

It is also essential simply to define the bulk $^{18}O/^{16}O$ ratio and $^{17}O/^{16}O$ ratio of the rocks and soils from Mars. This can best be done by analyzing a variety of rock fragments and different types of soils. Thus, it is important that sampling procedures be developed to obtain the widest variety of 0.5 to 1.0 cm-sized rock fragments and the greatest possible spectrum of depths in the Martian regolith. By comparing isotope studies on such materials with data previously obtained from the Earth, the Moon, and from meteorites, we may be able to draw some important conclusions regarding the origin and development of the solar system.

Note that the above-described experiments can be carried out on as little as 5 mg of a whole-rock sample or mineral separate. If we restrict the experiments to anhydrous minerals (quartz, feldspar, pyroxene, etc.), then the measurements will not be significantly affected by any sterilization treatment that involves simple heating to temperatures $\leq$ 300°C for a few days or a month. Even heating to 700°-800°C for a short time will probably not cause any drastic changes in $^{18}O/^{16}O$ of most anhydrous minerals. However, if the returned sample contains hydrous minerals or carbonates, such minerals will very likely be scientifically degraded to a certain extent by <u>any</u> type of heat treatment (particularly if the minerals are very fine-grained). Wherever there is loss of H_2O or CO_2 during heating there will be <u>some</u> shift in the $^{18}O/^{16}O$ ratio. Nonetheless, for a given mineral such isotopic changes are semiquantitatively predictable, and the magnitudes of the effects can be evaluated by making laboratory experiments on analogous materials, <u>if we know accurately the temperatures and times of heat treatment applied to the returned sample</u>.

Certain hydroxyl-bearing minerals (e.g., biotite, muscovite) will be much less affected by heat treatment at $\sim$ 300°C than will others such as clay minerals, so without knowing the mineralogical constitution of the Martian crust it is difficult to evaluate the experimental difficulties that will be produced by sterilization. Some clay minerals (e.g., montmorillonite) will partially dehydrate even at 25°C. However, if the sterilization temperatures can be kept reasonably low ($\leq$ 200°C) there is a very good chance that useful $^{18}O/^{16}O$ ratios can be obtained from almost all of the likely materials to be found on the surface of Mars. This will immensely strengthen our ability to make interpretations concerning the interactions between Martian volatiles (H_2O, CO_2, etc.) and the minerals or glasses that make up the Martian crust.

Oxygen isotope fractionations at low temperatures are very large; this feature means that oxygen isotope studies are particularly valuable in studying low-temperature processes such as weathering and hydration in terrestrial rocks, and in following the details

of the hydrologic cycle on Earth. To maximize our understanding of analogous processes on Mars, and to be able to more fully trace the history of volatiles on Mars, it would be most valuable to be able to analyze the $^{18}O/^{16}O$ ratios of various gases in a sample of the Martian atmosphere. Every effort should thus be made to return such a sample from Mars, and to keep it isolated from any gases released during sterilization heating of the returned solid sample. According to most evidence on the constitution of the Martian atmosphere, any such sample should contain sufficient CO_2 for isotopic analysis. On the other hand, the presumed atmospheric concentration of H_2O is so low that, if possible, a special sampling technique (e.g., some form of gas adsorption that does not involve any $\delta^{18}O$ fractionation) should be strongly considered for the Mars mission, in order to enable us to determine the $\delta^{18}O$ value of Martian water vapor. A water sample of at least 5 micromoles is necessary for a good $\delta^{18}O$ determination.

If sterilization of the Martian atmosphere sample is necessary, heating to 200°-300°C or above will undoubtedly cause some isotopic exchange among the gaseous molecules ($^{13}C/^{12}C$ and D/H effects would accompany the $^{18}O/^{16}O$ changes). However, if the overwhelmingly dominant constituent of the Martian atmosphere is CO_2, then the sample can safely be heated to very high temperatures without affecting either the $\delta^{13}C$ or $\delta^{18}O$ of the CO_2. The original isotopic record in the minor gaseous species will, of course, be destroyed during such treatment.

2. Hydrogen

Hydrogen isotope analyses of water vapor and hydrous minerals from Mars (in conjunction with the aforementioned $^{18}O/^{16}O$ analyses) should be very useful for the following reasons: (a) they may enable us to evaluate the contribution of deep-seated igneous H_2O (juvenile?) to the surface rocks and to the atmosphere. If high-temperature igneous or metamorphic minerals such as biotite are indeed found, comparison with the D/H ratios obtained on analogous samples from Earth will be very valuable, because to date no isotopic measurements on such extraterrestrial OH-bearing minerals have been made. (b) D/H data can aid in defining the total amounts of H_2O and hydrogen loss from Mars, as well as the degree of isotopic fractionation that has accompanied such escape. (c) D/H analyses are probably the only way to determine the overall contribution (if any) of deuterium-free solar wind hydrogen to the Martian atmosphere or surface. (d) They may help define the extent of formation of cosmic-ray spallation deuterium in Martian surface materials. (e) They will be very useful in tracing the hydrologic cycle on Mars and in interpreting the temperatures and the detailed mechanisms involved in hydration of Martian minerals and glasses.

All statements made above about the effects of sterilization on the $\delta^{18}O$ values of hydrous minerals apply equally well to the problems of hydrogen isotope determinations on such minerals. Any hydroxyl-bearing mineral that undergoes partial dehydration will also undergo a D/H shift. Many fine-grained clay minerals would be drastically affected at temperatures of 200°-300°C. However, if the evolved gases are retained in a sealed vessel and if D/H measurements can be made on such gases, it should be possible to reconstruct much of the useful isotopic information that could have been obtained from an unheated sample. If the sample return container can be made impermeable to hydrogen loss (sealed, gold-lined capsule?), then the D/H ratio of the bulk Martian sample can, in theory, be measured regardless of the type of sterilization heating. Even such a single measurement would provide a useful constraint on the history of Martian volatiles.

3. Silicon

The silicon isotope measurements of Martian samples will be important primarily in defining whether or not the whole-rock $^{30}Si/^{28}Si$ ratios on Mars are similar to those obtained on samples from the Earth, Moon, and meteorites (all of which are isotopically almost identical). Should Mars prove to be isotopically unique, this would have significant implications concerning the development of the solar system; thus, this is a potentially important measurement that needs to be made.

Fractionations of $^{30}Si/^{28}Si$ among coexisting minerals in terrestrial rocks and meteorites are very small. Thus, $^{30}Si/^{28}Si$ analyses of minerals will probably be of limited usefulness in solving Martian geochemical problems. However, extremely large ^{30}Si enrichments (accompanied by very large ^{18}O enrichments) have been observed on the amorphous coatings on grain surfaces of the lunar soils; these are produced by bombardments of the lunar surface with nuclear particles, micrometeorites and/or meteorites, but the exact mechanism is not fully understood. Such effects should be less important on the Martian surface, both because of blocking of incoming particles due to the presence of an atmosphere, and because of superposition of Martian erosion processes. Nonetheless, it will be important to search for these possible ^{30}Si (and ^{18}O) grain-surface enrichments, and comparison with the lunar samples may help elucidate the exact fractionation mechanisms.

Fortunately, the $^{30}Si/^{28}Si$ ratios are very insensitive to any type of heat treatment. The whole-rock $\delta^{30}Si$ values will not be disturbed even by melting the sample. It has already been shown, for example, that heating lunar samples to 650°C for 1-2 hours has no discernible effect on the pattern of ^{30}Si enrichments on

the grain surfaces (it also has virtually no effect on the accompanying $\delta^{18}O$ enrichments). Therefore, all of the significant silicon isotope measurements will be virtually unaffected by any conceivable sterilization procedure.

4. Carbon

Carbon isotope measurements have the potential of helping decide whether or not living organisms have ever been important on the surface of Mars, because appreciable ^{13}C fractionations are produced by animals and plants on Earth. Also, CO_2 has definitely been identified in the Martian atmosphere, so there is a reasonable possibility that carbonate minerals will be found on Mars. Measurement of $\delta^{13}C$ (and $\delta^{18}O$) of such carbonates will aid markedly in deciphering their origin and, possibly, their temperatures of formation. Comparison with $\delta^{13}C$ measurements of terrestrial and meteoritic materials will help in interpreting the entire carbon geochemical cycle on Mars. It is clearly important to obtain as much isotopic information as possible on all the forms of carbon that may be present in Martian samples (CO_2, carbonate, reduced carbon, organic carbon, etc.).

Most carbonate minerals resist decomposition at temperatures of 200°C or less. At higher temperatures, decomposition becomes important but, if the evolved CO_2 is preserved in a sealed container, much useful $\delta^{13}C$ information will also be preserved or may be readily inferred. Reduced carbon in terrestrial and lunar igneous rocks is also relatively insensitive to heat treatment at temperatures below 300°C. Marked evolution of such carbon as CO of CO_2 does not usually begin until temperatures are raised above 500°C.

Many of the carbon isotope differences that may be present in different coexisting organic molecules will probably be lost if sterilization is done at temperatures above 150°C. Therefore, depending on the relative proportions of carbonate carbon, reduced carbon, and organic carbon, it may be very difficult to reconstruct the original carbon isotope record, unless sterilization is done at quite low temperatures.

If the evolved gases are all preserved during sterilization, then a bulk $\delta^{13}C$ value can be determined on the entire Martian sample, regardless of the temperature of sterilization. Such an analysis would have some value, but it is very minor compared to the immense amount of carbon isotope information theoretically retrievable from an unsterilized Martian sample.

Isotopic measurements on carbon dioxide and carbon monoxide in the Martian atmosphere are important and should be made on a

separately preserved sample of the Martian atmosphere. Especially, this sample must be kept separate from the solid sample if any type of heat sterilization is used.

5. Sulfur

Sulfur isotope fractionations on Earth are very large, particularly between sulfate species and sulfide species; they provide significant information about terrestrial inorganic and bacteriological processes. Sulfur isotope fractionations among coexisting sulfide minerals are much smaller, but have nevertheless been used to estimate temperatures of formation of terrestrial sulfide minerals. The overall $\delta^{34}S$ values of meteoritic troilite and deep-seated igneous sulfides from both the Earth and Moon are very similar.

It is important to determine $\delta^{34}S$ values in a variety of Martian rock fragments and soils, for comparison with the data previously obtained from the Earth, the Moon, and meteorites. Such data are essential in trying to understand the geochemistry of sulfur and the sulfur cycle in the Martian crust. Important conclusions can probably be drawn about hydrothermal alteration processes and volatile transport in near-surface rocks on Mars.

Sulfur is not likely to be present in great abundance in Martian rocks, and that will restrict our ability to obtain data on coexisting sulfur-bearing minerals. However, even bulk determinations of $\delta^{34}S$ in sulfate and sulfide can be useful. Sulfide species, unfortunately, are very susceptible to alteration at temperatures as low as 200°-300°C in a hydrous atmosphere, so the sterilization procedure will provide important constraints on the usefulness of sulfur isotope data. Depending on the temperatures chosen, the alteration produced by sterilization may involve such effects as exchange of sulfur isotopes among coexisting minerals, destruction of sulfur-bearing minerals, and evolution of sulfur-bearing gases such as SO_2 and H_2S. If the gases can be collected for isotopic analysis, some critical scientific information may still be retrievable. Considerable laboratory experimentation utilizing the sterilization procedures on simulated Martian samples would be necessary to evaluate the data properly. Extreme sterilization temperatures ($\sim$ 1000°C) would destroy all useful $\delta^{34}S$ information except the overall $^{34}S/^{32}S$ ratio of the bulk sample. Loss of any of the gases evolved during high-temperature sterilization would make it totally impossible to obtain any useful $^{34}S/^{32}S$ data from the Martian samples.

HYPOTHETICAL STERILIZATION PROCEDURE*	OXYGEN ISOTOPES				HYDROGEN ISOTOPES		SILICON ISOTOPES		CARBON ISOTOPES			SULFUR ISOTOPES		
	Anhydrous Minerals	Hydrous Minerals	Carbonates	^{18}O Surface Enrichments	Whole* Rock	Minerals	Minerals & Whole Rocks	^{30}Si Surface Enrichments	Carbonates	Reduced Carbon	Organic Carbon Compounds	Sulfate Minerals	Sulfide Minerals	Whole* Rock
150°C/30 days	OK	OK?	OK?	OK	OK	OK?	OK	OK	OK?	OK	?	OK	OK	OK
200-250°C/7 days	OK	?	?	OK	OK	?	OK	OK	?	OK	NO	OK?	OK?	OK
300-350°C/1 day	OK	?	?	OK	OK	?	OK	OK	?	OK?	NO	?	NO	OK
700°C/1 hour	OK?	NO	NO	OK?	OK	NO	OK	OK	NO	?	NO	?	NO	OK
1000°C/5 min.	?	NO	NO	?	OK	NO	OK	?	NO	?	NO	?	NO	OK

* - Whole rock here means isotopic composition of the entire bulk sample returned, and the entire table is predicated on the assumption that during sterilization the evolved volatiles are quantitatively retained.

OK - Indicates sterilization will probably cause no analytical problems whatsoever.

OK? - Indicates sterilization may cause a few analytical difficulties, depending on the exact minerals present, and upon their grain sizes.

? - Insufficient information to decide whether sterilization will totally invalidate isotopic analysis.

NO - Indicates that sterilization will cause an appreciable or total ruination of the isotope analysis.

B. Age Dating

Information about the history of volcanic and metamorphic activity on Mars must come from the application to the samples of one, or preferably all, of the radioactive dating techniques involving the decay of a long-lived radioactive isotope (R) to a stable daughter product (S). The pairs (R/S) of isotopes which can be used are $^{235}U/^{207}Pb$, $^{238}U/^{206}Pb$, $^{232}Th/^{208}Pb$, $^{87}Rb/^{87}Sr$, and $^{40}K/^{40}Ar$. Each of these will be considered in turn.

1. ^{40}K-^{40}Ar and ^{39}Ar-^{40}Ar Ages

The $^{40}K/^{40}Ar$ dating technique yields only a lower limit to the formation time of a sample because of possible natural losses of the rare gas ^{40}Ar from the sample subsequent to its formation. The analysis of the total ^{40}K and total ^{40}Ar contained in a sample thus provides at least this basic information.

The $^{39}Ar/^{40}Ar$ dating technique, which is a variation of the K/Ar method, provides a way to avoid this limitation in many cases. Here, a portion of the ^{39}K is converted to ^{39}Ar by neutron irradiation. The Ar is then extracted and analyzed in steps of increasing extraction temperature. Sites within the sample which are easily degassed at low temperatures and have previously lost some ^{40}Ar will now contain Ar with a low $^{40}Ar/^{39}Ar$ ratio. Consequently, the earliest releases will have low apparent ages (corresponding to low $^{40}Ar/^{39}Ar$). The gases released at higher temperatures will be less and less affected by natural low temperature ^{40}Ar losses until, ideally, several release fractions are obtained which are unaffected and, thus, have the same $^{40}Ar/^{39}Ar$ ratio. The age corresponding to this plateau in the $^{40}Ar/^{39}Ar$ ratio is defined as the gas retention age; this age is unaffected by low temperature losses. It identifies a time of complete ^{40}Ar loss in a severe metamorphism or the time of formation of the sample, but no distinction can be made between the two possibilities. In the best circumstance, the $^{40}Ar/^{39}Ar$ technique can provide evidence for recent low temperature outgassing from a sample, the time of last severe degassing, and limits on the time of its formation. The $^{40}Ar/^{39}Ar$ plateau age provides a better lower limit to the formation age than does the total $^{40}Ar/^{40}K$ analysis if the age spectrum (a plot of apparent age vs. Ar released) can be physically interpreted. At the very least, the integrated Ar composition provides the same information as the total ^{40}K-^{40}Ar analysis.

Based on the consideration that only simple minerals are present that release Ar by diffusion according to Fick's law, losses of more than 10% of the ^{40}Ar begin to affect the plateau age. ^{40}Ar

losses of 50% lead to a plateau age lower by 25%. Losses greater than 50% destroy the plateau and yield even lower maximum ages. If a semblance of a plateau remains, a rough estimate of loss can be given. Thus, in evaluating the effect of sterilization procedures on age information obtainable by the $^{40}Ar/^{39}Ar$ method, losses up to 10% of the ^{40}Ar are acceptable, losses of 10-50% are manageable, and losses greater than 50% should be avoided if at all possible. These limits include previous natural losses and are thus upper limits for sterilization loss. Any sterilization losses of ^{40}Ar will seriously affect the record of comparable low temperature losses in the natural environment. In any case, the gases released during sterilization should be collected and analyzed for comparison with the results from $^{40}Ar/^{39}Ar$ analysis of the sterilized sample (particularly if it is possible that most of the ^{40}Ar were released during sterilization).

The table below shows the effects, in terms of fraction of ^{40}Ar lost, of heating several different types of samples in vacuum with the various temperature-time combinations suggested for sterilization. The table has been constructed from data available in the literature for lunar basalts and plagioclase (cf. Turner et al., 1973), the Bjurböle meteorite (Podosek and Huneke, 1973) and illite clay (Weaver and Wampler, 1970). In this table, OK refers to <10% ^{40}Ar loss, ? refers to 10-50% ^{40}Ar loss, and No corresponds to >50% ^{40}Ar loss. These losses, as described above, affect the extent of loss of information during sterilization.

Fractional release of ^{40}Ar

T °C	t sec	Fraction ^{40}Ar Released			
		Lunar Basalt	Lunar Plagioclase	Bjurböle Meteorite	Illite Clay
150	2.6×10^6	none (OK)	none (OK)	.001 (OK)	.004 (OK)
250	6.1×10^5	.004 (OK)	none (OK)	.008 (OK)	.064 (OK)
350	8.6×10^4	.015 (OK)	.001 (OK)	.029 (OK)	.264 (?)
700	3×10^2	.073 (OK)	.018 (OK)	.124 (?)	.945 (No)

Data on terrestrial basalt, rhyolite, hornblende, biotite, and muscovite (G. N. Hanson, letter in Appendix) show only up to 12% loss on heating in vacuum for one hour at 700°C. These losses are comparable to those for all but the clay sample shown in the above table. Thus, losses during this sterilization protocol from these and similar minerals would be considered acceptable.

The very few data available on illite clays suggest a much different situation for minerals with constituent H_2O and OH. Complete ^{40}Ar loss is obtained by 700°C, with as much as 10% loss at 250°C. Comparable illite data are presented by Evernden et al. (1960). The release of ^{40}Ar from glauconite and illite are similar, and major losses of ^{40}Ar from glauconite also occur with a loss of structural water (Evernden et al., 1960). Thus, structural changes, particularly those associated with water loss must be prevented if possible during sterilization. These occur over the range 200-400°C, and this puts strong limits on even low temperature sterilization procedures if these minerals are a major Mars soil constituent. Thus, detailed data are required for Martian analogues in which structural changes are expected before definitive limits on sterilization procedure can be given. High sterilization temperatures (>700°C) will certainly result in severe ^{40}Ar loss and would require collection and analysis of released ^{40}Ar in order to obtain a meaningful K/Ar age.

From the formal diffusion calculation used here, temperatures required for the loss over a five minute period of more than 90% of the ^{40}Ar from the lunar samples and meteorite are above 1150°C. This is higher than the temperature at which phase transitions, melting, and reactions between phases can occur, and little credibility can be given to the formal calculation. Temperature regimes marked by structural transitions should be avoided during sterilization.

It has been tacitly assumed that the $^{40}Ar/^{39}Ar$ variations are more a reflection of ^{40}Ar loss than of K redistribution or loss. In instances where mineral structure is changing, this is not a good assumption and must be explicitly determined for particular conditions. Again, a sterilization procedure causing structural changes should be avoided.

We note that in a polymineralic system, losses from one mineral may be extreme, while another may retain Ar and provide the desired information. A criterion for this is provided by association of chemical characteristics ($^{39}Ar/^{37}Ar/^{38}Ar$ ratios derived from neutron reactions on $^{39}K/^{40}Ca/^{37}Cl$ respectively) with portions of the age spectra. Serious interferences of Ar released from different minerals are reduced by analyzing separated minerals. Significant amounts of ^{40}Ar may be trapped and not be derived from in situ radioactive decay of ^{40}K, thus giving ages which will be too high. In principle, trapped ^{40}Ar can be identified through lack of correlation with ^{39}Ar produced from the K. No criteria exist for the effect of sterilization procedures on our ability to distinguish trapped Ar and, thus, the least severe sterilization conditions would be most desirable. Evidence for the existence of trapped ^{40}Ar may be lost if the age spectrum is severely

altered by sterilization losses. There may be corresponding amounts of trapped ^{36}Ar, which might provide a means of correcting for trapped ^{40}Ar even in degassed samples as long as sufficient variation still existed in the $^{36}Ar_{trapped}/^{40}Ar_{radiogenic}$ ratio.

These statements made so far refer to relatively simple, well-behaved systems. The application of the $^{40}Ar/^{39}Ar$ method to complex, polymineralic systems has given results that are not so easily interpreted and, in such instances, the age obtained is given only within the limits of uncertainty in the interpretation of the complex age spectrum. The complexity in observed age spectra has been reduced by the analysis of mineral separates and the association of a part of the age spectrum with a particular mineral. Analysis of separated minerals is strongly recommended for Mars samples. In several instances, even separated terrestrial minerals have failed to give meaningful age patterns. No systematics for predicting just which minerals will yield meaningful results have yet been established. Thus, every Martian analogue sample needs to be studied in detail by the $^{40}Ar/^{39}Ar$ technique.

Some minerals have given $^{40}Ar/^{39}Ar$ ages consistent with ages determined by other dating techniques. In the case of lunar and terrestrial samples, credibility of $^{40}Ar/^{39}Ar$ ages and the empirical systematics required to obtain meaningful ages, have been gained, in part, from these comparisons. At the present time, this avenue of approach should be followed in Mars sample and Mars analogue sample analysis to establish empirical bases for age interpretation.

The neutron irradiation required for $^{40}Ar/^{39}Ar$ analysis also generates detectable amounts of ^{38}Ar from ^{37}Cl and ^{37}Ar from ^{40}Ca. Analysis of the Ar isotopic composition of a neutron-irradiated sample provides at the very least a total K/Ar age as well as a measurement of ^{37}Cl, total trapped Ar, cosmic ray-produced Ar, and Ca. The cosmic ray exposure can be determined from the ratio of spallogenic Ar to the target Ca calculated from the $^{38}Ar_s/^{37}Ar$ ratio. All of these measurements require that significant amounts of Ar released during sterilization be retained if more than limits are desired.

2. I-Xe and Pu-Xe Dating

The early history of the solar system has so far been most clearly delineated by the study in meteorites of ^{129}Xe and fission Xe resulting from the decay of now-extinct ^{129}I and ^{244}Pu. The observation in the Martian samples of excess ^{129}Xe and ^{244}Pu fission Xe in Mars samples beyond that found in the Martian atmosphere would suggest the

formation of Mars materials at a time when these nuclei still existed. If excess ^{129}Xe is associated in situ with I and the ^{244}Pu fission Xe with U, then the early chronology of Mars samples can be determined and their formation at an early time definitively established. This correlation has been observed in meteorites, but not in lunar samples, by using a technique very comparable to that for $^{40}Ar/^{39}Ar$ dating. ^{129}Xe excesses are correlated in stepwise thermal release of Xe with ^{128}Xe produced from ^{127}I by neutron irradiation. ^{244}Pu fission Xe is correlated with fission Xe from neutron-induced fission of ^{235}U.

The Xe correlations in meteorites have been made only for the high (>1100°C) temperature Xe released (cf. Podosek, 1970). Comparable results from Mars samples would not be affected by brief heating in vacuum at temperatures below 1000°C. However, it is not clear what should be expected of Mars samples and it seems reasonable to accept the conditions for sterilization imposed by the $^{40}Ar/^{39}Ar$ dating technique as applicable to the I-Xe and Pu-Xe dating techniques. Structural changes in the minerals should be avoided.

The information on the existence of excess ^{129}Xe and ^{244}Pu fission Xe may be contained in atmospheric Xe or adsorbed or trapped Xe which may be degassed at low sterilization temperatures. The Xe released during sterilization should be collected for analysis.

3. Rb-Sr Dating

Very important information concerning the evolution of Mars may be obtained by application of the Rb-Sr dating technique. The method relies primarily on measurement of Rb and Sr concentrations and Sr isotopic compositions in rocks and in separated mineral phases of rocks. The most favorable circumstance would be one in which one or more rock fragments of mass $\gtrsim$ 100 mg were returned, in which case mineral isochrons could be determined, as was done for a 62 mg fragment of basalt returned by Luna 16 (Papanastassiou and Wasserburg, 1972). These ages would then determine one or more periods of Martian volcanic activity with direct implications for the thermal evolution of the planet. The Sr isotopic compositions existing in the magma at time of extrusion can also be determined by this technique. If the initial composition of Sr incorporated into Martian materials at the time of formation of the planet is known, inferences can be drawn about the Rb/Sr ratio in the source region for the rocks, and perhaps about its composition. The planetary initial Sr composition might be determined by measurements on fragments of old age and low Rb/Sr. More likely, the initial Sr composition would have to be assumed equal to the value found for the Moon and certain meteorites, and believed to be characteristic of the solar system at the time of formation of planetary bodies.

As we do not know the mineralogy of Martian rocks, it is difficult to assess the applicability of the method and its susceptibility to biological sterilization. However, it seems probable that, providing suitable samples are returned, it will be both applicable and insensitive to all conditions of sterilization except severe heating. In the case of the Luna 16 fragment, an age with a precision of ±5% was obtained for a 62 mg fragment of an ilmenite, plagioclase, and pyroxene rich rock in which the Rb/Sr ratio of the "total" sample was only about 0.003. The Luna 16 fragment was 3.4×10^9 years old. A 3×10^8 year old rock with the same enrichment in radiogenic ^{87}Sr would have to have Rb/Sr $\approx$ 0.4, not unusual for terrestrial rocks, but high for lunar rocks.

The information obtained from the mineral isochron technique could be destroyed by too severe a heat treatment, as that would cause migration of Rb and Sr between the mineral phases. Present data on thermally induced migration of Rb and Sr are meager, but serve to illustrate the type of effects to be expected. The following tables were compiled from literature data under the following assumptions: (a) that diffusion of Rb and Sr in mineral systems is adequately represented by the Arhennius equation $\frac{D}{a^2} = \frac{D_o}{a^2} e^{-Q/RT}$ where D is the diffusion coefficient, a the grain radius, D_o a constant, Q the activation energy of the process, R the gas constant, and T the absolute temperature; and (b) that the diffusion process is adequately approximated by isotropic diffusion from spherical mineral grains. These are severe approximations, but are made for reasons of simplicity. As may be seen from the tables, the system most susceptible to thermal-induced migration is that of Rb in glass. These data are appropriate for some of the lunar rocks, where much of the Rb resides in an interstitial glassy phase. A grain radius of 10μm is assumed as typical of this interstitial glass. If the calculations in the tables are valid, severe degradation of mineral isochrons may occur for temperatures as low as 250°C for heating times of one week. Experience indicates that this may be an unduly pessimistic estimate, but it points out the need for further experimentation to clarify this point. The negligible effect of any of the heating protocols on Rb in biotite (see table of Rb diffusion in biotite) is in qualitative agreement with an experiment on an Adamellite by Baadsgaard and van Breemen (1970) where Rb migration was detectable in biotite and muscovite only on heating above 800°C for periods of 100 hours. No attempt was made to correct the D/a^2 values in the tables to a common grain radius. Thus, the values in the second and fourth tables are those appropriate to the original experiments. A grain radius of 100μm is assumed in the calculations for the third table.

Rb diffusion in glass. Based on data of McVay and Day (1970) summarized in Compston et al. (1972). Extrapolated from 600-800°C.

T	t	D $cm^2\ sec^{-1}$	(D/a^2)* sec^{-1}	$\frac{Dt}{a^2}$	F**	Information Loss
150°C	30d (2.6×10^6 s)	10^{-17}	10^{-11}	2.6×10^{-5}	.017	nil
250°C	7d ($.6\times10^6$ s)	2×10^{-14}	2×10^{-8}	1.2×10^{-2}	.33	significant
350°C	1d (8.6×10^4 s)	5×10^{-12}	5×10^{-6}	43×10^{-2}	.99	total
700°C	5 min	10^{-7}	10^{-1}	30	1.0	total

* Assumes a = 10μ = 10^{-3} cm. Assuming a = 100μ = 10^{-2} cm decreases F by factor 10 in region where $F \approx 3.4\sqrt{\frac{Dt}{a^2}}$ ($F \lesssim 0.1$)

**F in the tables in the Rb-Sr and U-Th-Pb sections is the fraction lost from spherical grains corresponding to the $\frac{Dt}{a^2}$ values given.

Rb diffusion in biotite. Extrapolated from data of Hoffman and Giletti (1970) between 550°C and 700°C.

T	t	D/a^2 * sec^{-1}	$\frac{Dt}{a^2}$	F**	Information Loss
150°C	30d	6×10^{-16}	16×10^{-10}	10^{-4}	nil
250°C	7d	6×10^{-14}	4×10^{-8}	7×10^{-4}	nil
350°C	1d	1.5×10^{-12}	13×10^{-8}	10^{-3}	nil
700°C	5 min	4.4×10^{-10}	13×10^{-8}	10^{-3}	nil

* Here a is the radius of an assumed infinite cylinder; i.e., all transport is radial. The original authors chose a = 34μ.

** For spherical geometry. F should vary by a small factor for actual geometries.

Na diffusion in albite. Based on data of McVay and Day (1970) summarized in Compston et al. (1972). Extrapolated from 600-800°C. Probable upper limit for Sr in plagioclase.

T	t	D $cm^2\ sec^{-1}$	(D/a^2) * sec^{-1}	$\frac{Dt}{a^2}$	F**	Information Loss
150°C	30d	$6x10^{-22}$	$6x10^{-18}$	$16x10^{-12}$	10^{-5}	nil
250°C	7d	10^{-18}	10^{-14}	$6x10^{-9}$	$3x10^{-4}$	nil
350°C	1d	$3.4x10^{-12}$	$3.4x10^{-8}$	$29x10^{-4}$	0.17	significant
700°C	5 min	$6x10^{-8}$	$6x10^{-4}$	$18x10^{-2}$	0.89	total

* Assumes a = 100μ = 10^{-2} cm.

** For spherical geometry.

Sr diffusion in biotite. Hart et al. (1968).

T	t	D/a^2 sec^{-1}	$\frac{Dt}{a^2}$	F*	Information Loss	
150°C	30d	2×10^{-17}	5×10^{-11}	2×10^{-5}	nil	Model C**
		10^{-20}	2.6×10^{-14}	5×10^{-7}	nil	Model A
250°C	7d	5×10^{-16}	3×10^{-10}	6×10^{-5}	nil	Model C
		4.5×10^{-18}	2.7×10^{-12}	6×10^{-6}	nil	Model A
350°C	1d	4×10^{-14}	34×10^{-10}	2×10^{-4}	nil	Model C
		3.1×10^{-16}	27×10^{-12}	5×10^{-6}	nil	Model A
700°C	5 min	8×10^{-13}	24×10^{-11}	15×10^{-5}	nil	Model C
		4.3×10^{-13}	13×10^{-11}	10^{-5}	nil	Model A

* For spherical geometry

** Model A and C of Hart et al. (1968) for variation of temperature with distance from intrusive contact. Average grain size was about 0.8 mm.

Results in the third table indicate that significant Na diffusion in albite may occur for temperatures as low as 350°C. This system has been used by Compston et al. (1972) as an upper limit for Sr diffusion in plagioclase. The diffusion coefficients of Rb and Sr in natural biotite deduced by Hoffman and Giletti (1970) and by Hart et al. (1968) in the second and fourth tables are significantly lower than those of McVay and Day used in the other two tables. Although this may cast some doubt on the latter values, it still appears that Rb and Sr migration in minerals may occur at relatively low temperature and is a matter of concern if precise mineral isochrons are to be determined on sterilized samples. Rb volatilization (distinguished from intergrain migration) from lunar rocks only becomes detectable above 1000°C (Gibson et al., 1973).

Should no igneous fragments suitable for mineral isochrons be included in the returned sample, the information available from Rb-Sr measurements reduces to calculation of model ages for the material. These ages are somewhat ambiguous in interpretation but may yield an approximation of the average time of chemical differentiation for the material studied. This is particularly true if the material studied has a high Rb/Sr ratio and other geochemical evidence indicates that it was derived from a source of low Rb/Sr. Alternatively, if a model age is determined on an aggregate sample which can be argued to be an approximate average of crustal materials, it will give an approximation to the time of crustal differentiation.

As for all trace elements, it is important that the sample not be contaminated by Rb and Sr from the sample container and that cross contamination between materials in the sample return container be avoided. The latter might occur if, for example, a Rb-rich clay in contact with a rock fragment were heated to decomposition. This must be avoided!

4. U-Th-Pb Dating

The U, Th, and Pb isotopes provide a set of coupled radioactive parent-daughter relationships ($^{235}U/^{207}Pb$, $^{238}U/^{206}Pb$, $^{232}Th/^{208}Pb$) from which times of crystallization and subsequent metamorphism of rocks can be determined. The coupled Pb/U systems are particularly useful, since Pb/U fractionation must affect both ratios simultaneously and in the same way. Concordance of both ages suggests that the age represents a well-defined event. Discordant ages imply a disturbance of the system, and the times of disturbance can sometimes be inferred from the Pb/U systematics. In some instances, crystallization times and the composition of the initial Pb included at the time of formation can be determined from mineral isochrons obtained from Pb composition and Pb/U measurements on separated minerals of a single rock (cf. Tera and Wasserburg, 1972). Important constraints on Pb/U chemical fractionation during planetary evolution can also be determined from such data.

$^{206}Pb/^{207}Pb$ model ages (assuming undisturbed Pb/U evolution since the time of crystallization) can also be calculated in the absence of U measurements. This age is an approximate age in view of the possibility that the Pb/U system may have been disturbed and in view of the uncertain composition of the initial Pb included at the time of formation. $^{206}Pb/^{207}Pb$ ages do have the advantage that they should be invariant to changes in the U/Pb ratio caused by the sterilization procedure, however.

As for the Rb-Sr system, lack of information concerning the mineralogy of Martian rocks prevents conclusive statements on the precise effect of various sterilization protocols. Further, literature data on the diffusion of Pb in various mineral systems are sparse. The following table shows data inferred from the study of Hart et al. (1968) on the effects of diffusion in a natural environment on the various age dating methods. The data are for Pb diffusion in potassium feldspar. Plagioclase, another feldspar, is one of the important mineral separates used in the study of the U-Th-Pb system in lunar rocks. These data suggest that heating at temperatures below 350°C, even for rather long times, would cause negligible Pb redistribution, whereas temperatures of 700°C or higher would cause significant redistribution if applied for more than a few minutes. Thus, plagioclase-whole rock, U-Pb isochrons should be rather insensitive to the sterilization protocol. More data on this and other mineral systems are needed.

Pb diffusion in feldspar. Model A of Hart et al. (1968)*

T	t	D/a^2 sec^{-1}	$\frac{Dt}{a^2}$	F**	Information Loss
150°C	30d	10^{-46}	2.6×10^{-40}	5×10^{-20}	nil
250°C	7d	2.2×10^{-33}	1.3×10^{-27}	4×10^{-12}	nil
350°C	1d	3.6×10^{-24}	31×10^{-20}	6×10^{-10}	nil
700°C	5 min	7.4×10^{-7}	2.2×10^{-4}	.05	slight

* See footnote in preceding table (Sr diffusion in biotite).

** For a spherical geometry. Average grain size not given in Hart et al. (1968).

Recent experiments on the Apollo 17 "orange soil" show that 58% of the total Pb present could be extracted by heating at 500°C for 12 hours in vacuum (M. Tatsumoto, letter in appendix). Experiments by Huey et al. (1971) show that about 35-50% of the Pb in Apollo soils 10084 and 12020 was removed by heating at 700°C for 24 hours in vacuum. Further experiments need to be conducted to better define the threshold

for Pb volatilization, particularly for clay minerals which may be abundant in the Martian samples. It would be desirable to recover any volatile Pb released during sterilization from the walls of the sample container.

The Pb measurements are extremely sensitive to contamination and, thus, the construction and type of material used in the sample return container should be carefully considered. It has been pointed out (C. Patterson, letter in appendix) that fused quartz and FEP teflon are two substances which can be fabricated free from trace metal contamination. The feasibility of lining the sample container with one of these materials should be investigated. The return of a sample uncontaminated with terrestrial Pb would allow calculation of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ ages. These ages would be invariant to fractionation of U/Pb induced by the sterilization procedure. Further, the $^{238}U/^{204}Pb$ ratio would yield information on the ratio of refractory to volatile elements incorporated into Mars during its condensation.

It would also be important to measure certain radioactive transient members of the ^{238}U decay chain such as ^{234}U, ^{230}Th, and ^{210}Pb. Processes acting on the Martian surface may cause alteration of the normal equilibrium activities of nuclides in this decay chain. For example, ^{222}Rn escaping into the Martian atmosphere decays into ^{210}Pb, which returns to the surface. In this way, subsurface conditions and the presence of water may cause an excess or deficiency of the equilibrium amount of ^{210}Pb and other nuclides. Such ^{210}Pb in returned samples would also be sensitive to heat sterilization. The half life of ^{210}Pb is 22 years and, thus, it is a tracer for recent processes.

C. Measurements of Abundances and Isotopic Composition of the Noble Gas Elements (He, Ne, Ar, Kr, Xe)

1. Noble Gases in the Martian Atmosphere

Trapped planetary gases degassed from the Martian interior may exist in the Martian atmosphere. The Earth, Moon, Sun, and various classes of meteorites all possess characteristic elemental and isotopic abundance patterns of the trapped noble gases which reflect differences in the volatile components of materials that formed these objects. Measurements of such gases in the Martian atmosphere will give an indication of the general type of volatile material incorporated by Mars and will aid in the characterization of volatile species present in the early solar-planetary nebula. For example, lunar surface samples contain little, if any, trapped planetary noble gases, but large amounts of solar wind-derived gases. This fact reflects the large volatile-element depletion of the Moon and its lack of a significant atmosphere or magnetic field. The Earth's atmosphere and surface rocks contain

noble gases which have been highly fractionated relative to solar gases by as yet undefined processes. Various classes of meteorites contain still different noble gas components which can, at least qualitatively, be related to concentrations of other volatile elements and to the degree of meteorite metamorphism. The relationship of Martian noble gases in this sequence will be important.

The surface of Mars, unlike the lunar surface, probably does not contain large amounts of directly implanted solar wind gases. However, the atmosphere and cold traps on the surface may contain these gases, and precise measurements of the atmospheric gases may be required to separate planetary components from solar-derived ones.

^{40}Ar, ^{4}He, and fissiogenic Xe produced from decay of radionuclides of K, U, and Th in the Martian crust are also to be expected in the Martian atmosphere. ^{40}Ar degassed from the crust and interior may be a major constituent of the Martian atmosphere, just as it is in the Earth's atmosphere and in the degassing of the Moon. Abundance measurements of these nuclides should give an indication of relative abundances of their parent elements, the extent of degassing of the Martian crust, and of the long term stability of these chemically unreactive gases in the atmosphere.

2. Noble Gases in the Martian Samples

The ^{40}Ar, ^{4}He, and fission ^{136}Xe formed by radioactive decay in the crust all offer the potential for age dating of Martian rocks, surface deposits, thermal events, and the age of the planet itself. In the event that returned Martian samples represent young volcanics only a few million years in age, the ^{40}Ar and ^{4}He gas retention ages may be important measures of that age. Conversely, if the samples represent very old rocks exceeding 4,000 million years in age, measurements of ^{129}Xe and ^{136}Xe from the decay of the extinct radionuclides ^{129}I and ^{244}Pu become conceivable. Such measurements would be important in characterizing the age of the planet. The ^{40}Ar age dating technique is discussed in detail in an earlier subsection.

Noble gas nuclides are expected to be produced in both the Martian atmosphere and surface samples by cosmic ray-induced nuclear reactions. The atmosphere offers partial, but incomplete, shielding from galactic cosmic rays, and the energy spectrum of these particles at the Martian surface is expected to be comparable to that experienced by a number of meteorites and returned lunar samples which have been studied. Therefore, noble gas products of these nuclear reactions are expected to be present in surface samples

and, possibly, in the atmosphere. Determination of the isotopic pattern of these gases can, potentially, yield information on the past density of the Martian atmosphere, the extent of mixing of surface deposits, and possibly ages of major meteorite impact events.

The heavier noble gases may exist in occluded form or otherwise entrapped in hydrated or oxidized surface samples or be chemisorbed on surfaces of colder subsurface material. The origin of these gases could be any of those described above.

The nature of the expected noble gases on Mars makes it highly desirable to return two types of samples, one of Martian rocks and soil and one of the Martian atmosphere. If, by analogy with the Earth's atmosphere, the atmosphere of Mars contains approximately 1% Ar and proportionally similar amounts of Ne, Kr, and Xe, an atmospheric sample of a few cm^3 by volume would be sufficient for detailed analyses. However, a sample of the Martian atmosphere would also be valuable for other types of experiments (chemistry, stable isotopes, etc.) where a greater atmospheric volume would be required. For studies involving age dating, including crystallization ages and times of major impacts, rock fragments are more valuable. However, the concentrations of noble gases may be higher in the soil particles. Thus, both soil and rock fragments are valuable, especially if these represent a variety of rock types and ages. Subsurface as well as surface samples are useful.

Sterilization of a volume sample of the Martian atmosphere by moderate heating would not seriously affect the noble gases, assuming that no noble gas contamination is introduced during the heating. Sterilization of solid samples would degrade experimental information to varying degrees depending upon the nature of the sample and the time and temperature of the sterilization process. The deleterious effect of dry heat sterilization on noble gas experiments would be gas loss by the sample; in this regard, higher temperatures are more serious than are longer times. Therefore, lower temperatures for longer times are to be preferred. In any heat sterilization process, some loss of noble gases is to be expected. It is important to retain escaped gases within a closed sample container for subsequent analyses, rather than to allow the evolved gases to be lost to the vacuum of space. Some design should be made to allow the gases contained in the sealed, sterilization container to be withdrawn and analyzed after sample return. Noble gas contamination of the sample by degassing of the container during sterilization can be minimized by strong degassing prior to initiation of the mission.

D. Measurement of Concentrations of Nuclear Reaction-Produced Radionuclides

Galactic cosmic rays penetrate the Martian atmosphere to the Martian surface and, through high energy nuclear reactions, produce radioactive species in the atmosphere and in surface materials. Among the more scientifically valuable, long-lived radionuclides are the following: ^{14}C, ^{3}H, ^{10}Be, ^{22}Na, ^{26}Al, ^{39}Ar, ^{53}Mn, and ^{81}Kr. Determinations of the specific activities of these radionuclides can characterize the spatial and general nature of the cosmic rays which interact with the Martian atmosphere and surface. By comparing the activities of very long-lived nuclides (of the order of a million years) with those with mean lives of only a few years, any major changes in the density of the Martian atmosphere due to volcanic activity or other processes in this time interval could conceivably be detected.

Because they combine chemically with oxygen to produce H_2O and CO_2, ^{3}H ($t_{\frac{1}{2}}$ = 12 yrs) and ^{14}C ($t_{\frac{1}{2}}$ = 5730 yrs) may also be important tracers for the movement and residence times of these two important volatile compounds at the lunar surface. Both of these radionuclides have been used to monitor recycling times of terrestrial ground water and carbonate deposits. If H_2O and CO_2 prove to be reasonably abundant compounds in the frozen Martian subsurface soil, ^{3}H and ^{14}C may have similar applications to the Martian surface. A comparison of ^{3}H and ^{14}C in atmospheric and subsurface materials would be particularly valuable.

Radionuclides produced by cosmic ray interactions with the Martian surface can also act as monitors for the extent of surface mixing. Certain stable nuclides produced by cosmic rays, such as isotopes of Sm, Gd, and the heavy noble gases, can also provide values for important parameters in characterizing mixing with depth sensitivities of up to several meters. A fairly large amount of information has recently been acquired about the degree of mixing of lunar surface fines through application of these measurements.

It deserves emphasis that the Gd and Sm isotopic shifts due to the capture of cosmic ray-produced neutrons will be unaffected by <u>any</u> sterilization procedure. Thus, regardless of procedure, information about cosmic ray exposure of Martian surface material and inferences about the mixing of Martian soils can be obtained from the measurement of the isotopic composition of these two rare-earth elements.

For ^{3}H and ^{14}C, just as for noble gases, atmospheric samples would be needed. For all radioactive and stable nuclides produced through cosmic ray interactions (including thermal neutron capture), surface samples of known variable depths relative to the Martian surface are most valuable. Both soil and rock samples are important.

The radionuclides ^{3}H and ^{14}C would be readily lost by heating of the sample during sterilization at temperatures ranging from that at the Martian surface to only a few hundred degrees if they are present as H_2O, CO, CO_2, or other relatively volatile compounds. If hydrogen and carbon are present in only trace amounts in the silicate structure, the loss is expected to be less severe. Loss of ^{39}Ar and ^{81}Kr would resemble loss of ^{40}Ar and the heavier, cosmic ray-produced stable noble gas isotopes. Loss of the other radionuclides during heat sterilization is not expected to be large at temperatures of the order of 200-300° unless the Martian sample undergoes appreciable chemical and phase changes. Sterilization in any gas medium that would induce chemical reactions within the sample should be avoided. Even if some radionuclides are partially degassed from the sample during heat sterilization, these radioactivities still constitute valuable information. Therefore, heat sterilization should be conducted in a closed container with a means of sampling any volatilized radionuclides.

Probable effects of dry heat sterilization.

	∿150°C ∿30 days	∿250°C ∿7 days	∿700°C ∿100 sec.
Trapped planetary and cosmic ray-produced noble gases in silicate structure	small	small	small-appreciable
Occluded and chemisorbed noble gases, including "ices"	?	appreciable	large
^{3}H, ^{14}C as frozen or adsorbed H_2O, CO_2	appreciable?	appreciable	large
^{3}H, ^{14}C, ^{37}Ar, ^{81}Kr in silicate structure	small	small?	appreciable?
^{22}Na, ^{26}Al, ^{10}Be, ^{53}Mn in silicate structure or clays that do not undergo major phase changes	small	small	small?
Gd, Sm isotopic composition	small	small	small

PHYSICAL PROPERTIES

A number of measurements of physical properties are suggested in this section, and statements concerning the deterioration of data subsequent to a possible heat sterilization are made. The discussion is largely centered around scientific problems rather than experimental methods. A the end of the section is a tabular summary of the effects of heat sterilization on the various experimental techniques.

A. Was There Ever a Magnetic Field on Mars?

With the finding of evidence for an ancient magnetic field on the Moon, it has become increasingly important to continue the search on other planets using returned samples. The existence of a fossil field and the dating of this field would provide considerable information on the thermal history of the planet. If the field can be ascribed to a core acting as a dynamo, then knowledge may be gained concerning the early differentiation history of the planet.

Prior to the return of lunar samples, there was no evidence for a remanent field on the Moon, since the actual field was too small to be detected by previous orbiting vehicles. A similar situation may apply to Mars at present, although there is equivocal evidence for a small Martian field (Dolginov et al., 1973). It is therefore of great interest to search in the Mars samples for signs of a natural remanent magnetization (NRM). This needs to be checked in the laboratory for stability by alternating field and thermal demagnetization. Rock samples a gram or more in size are ideal for this purpose, although smaller chips could be used. There are two problems that would result from heating the samples for biological sterilization. First, some material may acquire a non-Martian magnetization when heated and cooled in the presence of a field. For example, very fine-grained iron can have blocking temperatures of 100°C or less; goethite magnetizes on cooling from above 120°C; and troilite magnetizes on cooling from above 320°C. Second, it may be impossible to heat the samples significantly without changing the magnetic carriers. For example, the reaction goethite → hematite occur at 350°C in air; fine-grained iron can grow and acquire a field at temperatures perhaps as low as 150°C; and the alteration of fine-grained or amorphous iron hydroxides can occur at temperatures significantly less than 350°C. The important issue requiring carefully planned analog studies is to understand clearly the magnetic overprinting that might occur by heating a sample significantly above the Martian surface temperature. Care should be taken to insure that the samples are not exposed to magnetic fields on the spacecraft or on return to Earth which are significantly greater than that of the Earth's.

B. How is the Iron Distributed Among the Various Phases?

It is possible to conduct the following, high magnetic field experiments in the laboratory by these methods: (a) hysteresis measurements, (b) high temperature studies, and (c) low temperature studies. In terrestrial samples, these measurements are useful in identifying magnetite (Tc ∿580°C), hematite (Tn ∿670°C), ilmenite (Tc ∿57°K), and the various Fe-Ti-oxide solid solution series, as well as goethite and lepidocrocite. It is also possible to learn something about the grain size distribution of the particles. In lunar samples, the dominant mineral of relevance is metallic iron. Magnetic methods have been specifically useful in measurement of the amount and the grain size distribution of that material. From the redistribution of iron, it is possible to infer a good deal about the time-temperature history of the regolith and the amount of meteoritic infall. The oxidation state of the iron-bearing minerals on Mars is not known. These measurements should, however, be useful as adjuncts to the mineralogy and to help identify the remanence carriers.

It would appear that heating to temperatures below the dehydration temperature would not upset these observations greatly. However, temperature is not the only parameter of concern. The atmosphere during heating is also important. Unfortunately, we cannot evaluate the most desired atmosphere constraints without further knowledge.

C. Bulk Physical Properties of Soils (Thermal and Electrical) or, How Can the Radar, Thermal Emission and Thermal Response of Mars be Interpreted?

From remote observations of planetary surfaces it has been possible to infer much about the nature of thermal and electrical conduction in the surface layers. When the thermal and electrical properties of returned lunar samples were measured in high vacuum conditions, they confirmed these early findings in a spectacular manner. Extending these studies to the Mars surface is not a simple matter, however, because (a) the dielectric constant determined by radar studies implies that there are large areas of both rock and soil, (b) the effect of gas on thermal conductivity in soils is only poorly understood, especially since we do not know how porous the Mars surface is, (c) the effect of monolayers of water on these properties at Martian surface temperatures is not well understood, and (d) local pockets of higher water content or permafrost may be present. The return of a sample from Mars should be specifically designed to answer questions about the moisture and volatile contents in the soil. With that information in hand, it will then be possible to determine the properties of relevant terrestrial analogue studies under those same conditions. If the quantity returned is large, it would be useful to make measurements on the actual Mars samples.

The adequate characterization of the nature and concentrations of moisture and volatiles in the Mars soils is of prime importance to an understanding of the physical character of the Martian surface. In addition, the presence of clay minerals may have a profound effect on these properties, so that it is desirable to preserve the clay minerals in their original state. Ideally, the sample should be returned frozen so that the full range of the effects of moisture on these properties can be studied. Specifically, it is of interest to measure the dielectric constant and loss tangent over a range of frequencies, the D.C. conductivity, and the thermal diffusivity. The seismic velocities and Q values of the same materials would be of general interest.

D. Optical Properties, or the Mapping of Mars by Spectral Reflectance

Much of our present information and understanding of the surface of Mars has been derived from remote telescopic and imaging probes using reflectance properties. It is therefore important to make measurements of the spectral reflectance of samples which are in as nearly a pristine condition as possible. With this knowledge, it may eventually be possible to map the weathering state over a wide part of the Martian surface. It has been suggested that the reddish color at the Martian surface is related to the presence of iron hydroxides. In the lunar material on the other hand, glass content plays a dominant role in determining the spectral properties. Heating of fine-grained or amorphous hydroxides above about 200°C will dehydrate them and modify their spectral reflectances. If the effects of glass are dominant, serious changes in spectral reflectance would occur at temperatures above about 400-500°C. In order to determine whether color is changed on heating, relevant experiments in controlled environments would have to be conducted.

E. What is the Seismic and Electrical Structure of the Deep Interior?

In considering the bulk properties of Mars, such as will be elucidated to some degree by the seismometer on Viking and from magnetic responses, some thought should be given to a study of the seismic and electrical properties of representative Mars samples. After the samples have been fully characterized, there may appear to be materials which could represent major geologic units. Measurements of seismic velocity and electrical conductivity as a function of temperature and pressure on terrestrial analogues should then be conducted.

F. Fission Tracks

Tracks resulting from spontaneous fission of U, Th, and Pu nuclei can be observed microscopically after the surface of a mineral grain

is etched with a solvent. Similarly, tracks produced by neutron induced fission of a radiogenic element during reactor irradiation can be observed in Lexan plastic placed adjacent to the sample. A great advantage of the method is the extremely small quantity of sample required.

Track studies on terrestrial and lunar samples and meteorites have shown that the following types of information can be obtained: 1) Location and concentration of certain radioactive elements (e.g. U) within a sample; 2) Determination of crystallization or metamorphic ages in very small samples from track density about concentrations of radiogenic elements. This method is important for studies of terrestrial rocks but has not proven very useful for lunar samples due to the high density of cosmic ray produced tracks; 3) Determination of cosmic ray flux and the identifies of the track-forming elements. Information on time of exposure to cosmic rays can also be obtained; and 4) Nature of cosmic ray induced radiogenic spallation products.

All of the above studies could be done on a returned Martian sample. The present Martian atmosphere would largely shield the surface from solar flare bombardment so that amorphous coatings on grains due to solar wind bombardment would probably be absent (P. B. Price letter, Appendix II). It appears that the atmosphere would also shield the surface from low energy cosmic rays so that tracks formed by radiogenic elements would not be obscured as in lunar samples (P. B. Price letter, Appendix II). Fission track dating could therefore be done and a better understanding of high energy cosmic rays could be gained.

A search could be made for rare grains with steep track gradients which, if found, would presumably have been produced when there was no Martian atmosphere (P. B. Price letter, Appendix II). Paleovolcanism and soil transport could be studied by fission track dating of individual grains. Both heavy particle tracks and spallation-produced isotopes could be studied to provide information on surface exposure times and erosion rates of samples.

A stratified sample such as a core might allow study of the variation in total atmospheric pressure with time, since the extent of atmospheric shielding is a function of the atmospheric pressure. Greater shielding would produce a more reduced ratio of tracks to spallation products and gives a characteristic change in the fossil track spectrum (R. E. Arvidson letter, Appendix II). The thin Martian atmosphere and relatively weak gravitational field may permit relatively soft and unablated landings of cosmic dust that could be identified by solar wind coatings and solar flare tracks. In areas protected from particle movement there may be a sedimentary history of cosmic dust fluxes (P. B. Price, letter, Appendix II).

The extent of heat sterilization of a returned sample would markedly affect the amount of information that could be gained from fission tracks. The ease of annealing of tracks within a mineral is proportional to rates of self-diffusion of elements within the mineral. As a general rule, the harder a mineral is and the higher its decomposition temperature, the greater is its resistance to track annealing. Large effects should not be noticed in most minerals below 150°C, and very noticeable effects should be observed at 350°C in a day (R. Walker and C. Naeser letters, Appendix II). The latter treatment would degrade the information to be obtained but would not totally erase it, especially in minerals from basaltic and high-grade metamorphic rocks. A summary of track annealing temperatures is listed in the table below. Lower temperatures for longer times would have a similar effect. For example, apatite held at 225°C for 10^4 min. (6.9 days) would also be partly annealed (Naeser and Faul, 1969). The effect of heat sterilization in the presence of H_2O vapor would be to markedly increase track annealing rates.

Further work is required on the kinetics of track annealing, especially the clay minerals. While it is unlikely that montmorillonite and other clay minerals can be etched, some research should be done on clay minerals to determine whether or not useful data can be obtained from them if they should be present in returned Martian samples.

Track reduction would begin after one hour at:

100°C	Basaltic glass	MacDougall, 1973
	Lunar impact glass	Fleischer and others, 1971
200°C	Feldspar glass	Fleischer and others, 1968
	Basaltic glass	Fleischer and others, 1969
300°C	Apatite	Naeser and Faul, 1969
	Lunar impact glass	Fleischer and Hart, 1973
400°C	Phlogopite	Maurette and others, 1964
	Muscovite	Fleischer and others, 1964
500°C	Pyroxene (pigeonite)	Fleischer and others, 1965a
	Olivine	Fleischer and others, 1965b
600°C	Sphene	Naeser and Faul, 1969
	Diopside	P. B. Price (written comm., 1974)
	Epidote	Naeser and others, 1970
	Garnet	P. B. Price (written comm., 1974)
700°C	Zircon	Fleischer and others, 1965b
	Feldspar	Fleischer and others, 1965a

G. Thermoluminescence

The main purpose in studying the thermoluminescence (TL) of a sample is to gain information on its thermal and radiation history. The radiation received by the sample from cosmic rays and solar particles, in addition to that from internal radioactivity, leads to electrons being trapped in energy levels in the "forbidden" band gap of the solid. Ambient temperatures on the planet can cause some of the electrons to be released from these traps. By studying the increase in trapped electrons as a response to intensity of radiation and their release in response to systematic heating, information on radiation-filling and thermal drainage should be obtained. From these studies, the γ-ray equivalent dose of radiation can be determined and, hence, a radiation history can be obtained for a given sample. The technique has been applied successfully to lunar samples. One of the most important kinds of information that can be obtained from thermoluminescence studies is the depth of burial of a sample below the surface; this can be calculated from determination of the effective storage temperature for the electron traps.

The Martian atmosphere should virtually filter all solar flare material and low energy cosmic rays out of the Martian surface (P. B. Price letter, Appendix II). On the other hand, since the maximum temperature on Mars is significantly lower than that on the moon, a much greater proportion of trapped electrons should remain stored. If a deep core sample were to be returned from Mars, thermoluminescence could be used for determining depth of origin of the material in the core and potentially for heat flow data (R. E. Arvidson letter, Appendix II). If, on the other hand, the sample were collected from the surface or near the surface, the measurements have less direct, obvious uses.

Thermoluminescence measurements are affected by any heat treatment. Heating above 100°C significantly compromises any measurement (R. E. Arvidson letter, Appendix II). Penetrating radiations also seriously affect data that can be obtained. Even exposure to visible light degrades the results, and sampling is ideally done in red light (R. E. Arvidson letter, Appendix II).

Further work should be done on appropriate materials and at varying degrees of thermoluminescence intensities at a variety of temperatures in order to determine the exact amount of sample degradation on heating. This can best be done after a Martian sample is obtained and studied.

Effects of Heating on Physical Properties

Track Studies	- See previous table.
Thermoluminescence	- Heavy loss for T > 100°C.
Magnetic Remanence	- Induces mineralogic changes: - grain growth - dehydration - oxidation
	- Heating over Curie points (120°C, 320°C, etc.) causes serious degradation.
	- Heating over 100°C may allow development of partial thermoremanence.
Magnetic Mineralogy	- Causes mineralogic changes: - grain growth - dehydration and phase changes (see mineralogy-petrology section).
Bulk Soil Properties - Thermal - Electric - Elastic	- Important to have a knowledge of the moisture and volatile content in the soils in situ in order to perform relevant analogue experiments -- heating will seriously compromise this.
Optical Properties	- Avoid mineralogic changes, especially dehydration.

GENERAL CONCLUSIONS

Mike Carr (Appendix II) points out the great importance of returned samples for understanding planetary evolution.

> "The analysis of returned lunar samples has completely transformed our concepts of how the Moon formed and what its subsequent history has been. Our present knowledge of the timing of events that led to the Moon's present configuration, the evolution of the crust, the bulk and trace element geochemistry and how it differs from that of the Earth have all been derived from examination of returned samples. The degree to which this understanding could have been achieved solely by remote analysis is a matter of conjecture but there is ample reason to be skeptical. Having lunar samples in hand allowed the complete analytical and intellectual capability of the scientific community to focus on the problem of the Moon's evolution. Instead of having a small pre-determined set of analytical techniques applied to the samples, the approach could be both all-encompassing and flexible, the analytical emphasis shifting as the meaning of each set of results become better appreciated. There is no reason to believe that these enormous advantages of returned samples should be any less for Mars. Indeed the apparently more complex geology of Mars enhances the importance of the kind of comprehensive examination that a returned sample allows."

This is not to demean the value of remote analysis. It is assumed that the mission design and execution will take cognizance of all available data relevant to the composition, physical state and geologic context of the Martian surface and the site from which the sample will be collected.

A. Sample Acquisition and Supporting Data

It is difficult to envision a returned Mars sample whose study would not add greatly to our knowledge and understanding of the planet and the Solar System. On the other hand, judicious selection and processing of the sample during acquisition may enormously enhance its scientific value. Although some of the improvements over a single, simple device suggested below may be incompatible with one another, each has sufficient merit to warrant serious consideration. We have not attempted to prioritize these alternatives; that must wait until more is known about Mars (from Viking, principally) and the actual constraints to be imposed on a sample-return mission.

If the returned Martian sample is sterilized, much potential information will be lost. However, some of that information may be recovered if the time-temperature-pressure conditions are continuously

monitored during sterilization and on the entire Earth return trip. Every effort must be made to keep the sample at its temperature of collection on the Mars surface. If sterilization is necessary, the sample should be cooled afterward to that temperature for the duration of the flight to Earth.

Experience with both lunar and terrestrial rocks has shown that particles greater than about 2 mm in diameter are required to yield sufficient details to permit truly fruitful interpretations, even if the rocks are texturally quite fine-grained. On the other hand, very large fragments are often wasteful of sample mass in terms of information returned. The chief constraints appear to be that some fragments must be large enough for mineral separation for age dating and for determining their petrologic textures. A 2-cm fragment meets these requirements. Relatively few experiments are eliminated or seriously compromised if fragments larger than 2 cm are not included in the returned sample, and the loss of those is more than offset if a variety of smaller fragments is returned instead of one or two larger ones. In order to assure that the sample contains abundant fragments of useful size (assuming that they are present in the vicinity of the lander), we strongly recommend that the sample-acquisition mechanism have the capability to enrich the collected material in particles 2-20 mm in diameter. This might be accomplished by a sieving or raking device, when used in conjunction with a more general sampler, because acquisition of a sample with a more nearly representative size distribution is also essential (i.e., a typical soil sample).

The keys to many important questions regarding near-surface processes and the recent erosional-depositional history of Mars may lie in the fine-grained stratigraphy of surface materials. Some specific questions and properties include depth of weathering, cosmic-ray studies, thermoluminescence, turn-over rate, and the depth of condensation of volatiles. The mode of collection most likely to preserve the stratigraphic details sufficiently well to permit such studies is coring. We recommend the consideration of a coring device capable of obtaining as long a core as possible (of the order of 1 m).

For several reasons, it would also be desirable to collect a variety of sub-samples from different locations and depths in the immediate vicinity of the lander and, if possible, to maintain these samples separately from one another. One mechanism for accomplishing this might be a scoop-type sampler similar to that to be used on Viking '75. This capability helps to insure the acquisition of a useful sample even if sampleable material is but sparsely and erratically distributed in the sampler field. Used in conjunction with an imaging system, it would also permit selection of sample characteristics for maximum scientific return.

It is clear that thermal treatment may release substantial quantities of adsorbed and chemically bound volatiles to the Martian atmosphere enclosed with solid samples. The most crucial measurements to be made on the atmospheric portion of the sample are the isotopic ratios of H and C (Appendix II, letter from T. Owen), and these would be the most severely affected. It is therefore important to provide for a separate sample of the Martian atmosphere that is kept separate from the solid surface sample.

Although auxillary scientific investigations should obviously be subordinated to the prime goal of obtaining and returning a sample of Mars surface material, we feel that much valuable science will be gained with the addition of landed imagery and the capability to direct the sampling device in response to it. Not only would imagery of the sampled environment greatly enhance the scientific interpretation of laboratory studies, but it could prove essential to assuring that a usable sample is obtained. It is needed in order to select different spots in the sample field for sampling. Visual imagery could also be important in assuring the safety of a sampling device if obstacles exist in the sample field.

The options listed above should be seriously considered as early planning for the mission is begun so that the constraints they impose on the mission can be better understood. Under no circumstances should our desire for the above-mentioned devices, valuable as they would be, be construed as implying that a lesser mission would not be of great scientific value. The scientific return from the 5 grams of lunar material from the Luna 16 and 20 missions acquired by American scientists (Earth and Planetary Science Letters, 1972, vol. 13, no. 2, 244 pages; Geochimica Cosmochimica Acta, 1973, vol. 37, no. 4, 390 pages) is clear testimony to the value of even a very small, undocumented sample. It is nevertheless hoped that the mission to collect a Martian sample will be designed to assure the highest feasible scientific return.

B. Landing Site: Conditions and Constraints

While it is obviously premature to make specific recommendations of areas or localities on Mars from which a sample should be obtained, certain general characteristics of sample sites can be recognized, and their consequences inferred. We recommend that a Martian sample return mission be targeted to collect as wide a variety of materials as possible. This type of sample would allow the study of a wide range of Martian processes and materials. We further recommend that every effort be made to assure that the sample contains volcanic rocks (in order to study Martian interior structure, chemistry and time scales for vulcanism) and materials that display a wide range of weathering conditions (in order to study Martian surface processes and environments).

If a capability for precise targeting and pre-landing site certification exist, it may be useful to consider briefly the site characteristics that would have desirable properties. The site should have a heterogeneity of surface materials, and indications that it represents a locus of accumulation of transported debris. Based on our current understanding of Mars, a canyon-mouth area would be such a site. Other things being equal, the vicinity of apparently young volcanoes would seem to favor the acquisition of fresh volcanic materials. We emphasize that these criteria are based on our current knowledge of the planet, and should be continuously updated as we learn more about Mars.

C. Effect of Possible Biological Sterilization

It would probably not be possible to destroy all of the interesting information in a Martian sample by any method of biological sterilization. The value of the sample can be severely compromised, however, depending on the nature of the sterilization process. The effects are complicated and depend on the nature of the sample. The reader must consult the body of this report in order to understand the scope of the problem. Some brief comments are given below.

If the returned Martian sample consisted or primary, dry silicate minerals (such as feldspars, pyroxenes, olivines, and oxides), the sample could withstand moderate temperatures of sterilization (about 200 to 300°C) without major loss of information. At slightly higher temperatures (about 400 to 500°C) oxidation-reduction reactions would begin and the more volatile elements would migrate. As sterilization temperatures increased, more and more chemical and isotopic systems would become unstable, until melting occurred at about 1100 to 1300°C, when all data except those on bulk composition would be lost.

Further consideration of the effects of sterilization is highly model dependent and must be constantly re-evaluated as new and improved data concerning the surface of Mars become available. Materials such as secondary hydrates, carbonates, organic compounds, "ice," various water-soluble or effluorescent minerals, and hydrated amorphous and glassy materials will start to break down under various pressure conditions temperatures as low as 100 to 200°C (see table in section on Mineralogy and Petrology). The products of these breakdowns would react with the primary silicates and oxides and, in the process, could seriously disrupt the various chemical, isotopic and physical systems. The extent of the damage is strongly dependent on the temperatures and times of sterilization as well as on the exact nature of the materials in the sample.

D. Recommendations for Sterilization Procedures

Hopefully, sterilization will not be required. From the point of view of extracting scientific information, sterilization is at best a necessary evil regardless of the method used. More acceptable than sterilization of the whole sample would be the return of a split sample, half of it sterilized and the other half not, to be opened after an evaluation of the biological hazard could be made. The following guidelines apply to a sterilized sample.

We believe that the following important features can be satisfied by a sterilization procedure, independent of the exact times and temperatures of heating that are finally deemed necessary.

1. The container should probably be made of some tough, durable material such as stainless steel. It should have as foolproof a seal as is possible to make and should be able to withstand internal pressures of at least a few hundred bars. The gases evolved during heating must be preserved in some manner. Inert chemical liners such as fused quartz or gold (or teflon, assuming sterilization temperatures are low enough) should be considered. Differential loss of hydrogen during sterilization is an important consideration, because changes in the state of oxidation of the sample would severely impair interpretation of magnetic and of certain mineralogical properties. Such changes can be minimized with a gold liner. No single liner material is acceptable for the whole range of scientific experiments. Gold is best for hydrogen retention, but it entails contamination with siderophile elements, and so on.

   In any case, material used to line the interior of the container must in no way interfere with the ability to provide a reliable seal.

   Whatever material is used for the container, it should be thoroughly degassed by thermal cycling prior to use and should be as free as possible from any source of contamination of important trace elements. Some mechanism should be incorporated to allow withdrawal of gases after sample return, and the container should be designed in such a way that volatile coatings condensed on the interior walls as a result of sterilization can be recovered and examined.

2. The container must, of course, have some pressure release mechanism for safety if there is any danger whatsoever that internal pressures will exceed the strength of the seal. Retention of the gases evolved during sterilization has extremely high priority, but it obviously must not be allowed to interfere with preservation of the solid sample.

Gases released after break of the inner seal should be absorbed on a series of appropriate getters present within the larger, sealed sample container.

3. Some attention should be paid to the possibility of chemically or physically removing the evolved gases from contact with the solid sample during the sterilization procedure. This may be desirable to prevent dissolution, re-hydration, re-carbonation and possible formation of new chemical compounds in the sample. Such a feature might make a pressure-release safety valve unnecessary, but it is not essential, and it must not be allowed to interfere with preservation and recovery of the evolved gases in such a way that isotopic and chemical information is lost.

4. A sample of the Martian atmosphere should be obtained and should be kept physically separate from the solid sample and from the gases evolved from the solid sample during sterilization.

5. Whatever the conditions of the sterilization procedure, the temperature-time history should be kept as simple as possible and should be carefully monitored and recorded. Ideally, this would involve heating at a single, specified temperature for a fixed length of time. Knowledge of the temperature-time history of the sample is critical in evaluating the original character of the Mars sample prior to sterilization, inasmuch as similar laboratory experiments will have to be carried out on analogous materials on Earth.

6. The temperature of sterilization should be kept as low as possible. Longer times are preferable to shorter times at a higher temperature.

7. No extraneous material of any kind should be added to the sample in some misguided effort to promote sterilization. This most particularly applies to addition of H_2O. Dry heating is preferable to wet heating even if slightly higher temperatures must be used. Heating in a humid atmosphere would promote isotopic and chemical exchange among minerals, would tend to destroy some minerals and form new ones, and in general would result in greater alteration of the original sample and more loss of scientific information. We realize that dry heating will dehydrate certain clay minerals irreversibly, but this is by far the lesser evil, because it should be possible to reconstruct the nature of the original clays from their decomposition products, provided that the volatiles released during sterilization are retained for analysis.

Of course, the sample collected could itself be very humid or contain ice and large amounts of thermally unstable materials. This could result in considerable pressure build-up during heating which would be undesirable (see Min-Pet report, Table II). To prevent this, the pressure release mechanism in the inner container should be set to a maximum of no more than a few dozen bars.

E. Experimentation in Preparation for a Returned Mars Sample

Preparations for the investigation and analysis of the returned Mars sample fall into two general categories as follows: 1) improvement and up-grading of analytical techniques and 2) simulation experiments to help interpret sample data. The identification of all of the reasonable areas of effort for development of analysis techniques is a large task and probably is worthy of a separate study. A partial list of these investigations is included below. No priorities should be inferred from the order in which the tasks are listed.

Many of the techniques used for the study of lunar samples will have to be modified to consume less material or be improved to gain more information from smaller particles in this small and extraordinary sample. It is, therefore, critical that laboratories presently doing the best job of petrological, geochemical, and geophysical analysis continue to be supported, both to keep a knowledgeable, up-to-date community of scientists and to further the state-of-the-art in analytical capabilities of all pertinent types. The tasks listed in the accompanying table are a few that need extra impetus at this time. The value of those development efforts are not greatly dependent on any special model of the Martian surface but are generally applicable

Pre-return Analytical Development

1. Chemical analysis of H_2O, CO_2, N_2, S, halogens, and platinum group elements.

2. Facility and techniques to handle and analyze (chemically and physically) small (1 to 10 micron) fragments.

3. Design and construction for a Mars sample return container. This study should include the material(s) that the container is constructed from, the nature of the seal, the nature of pressure release valves, mechanisms for temperature control, and gas adsorbers.

4. Mineral separation techniques to avoid elemental exchange, structural modification and sample degradation during separation.

Simulation studies should be limited to the most critical until more is known about Mars. After the actual sample return, a rather complete series of experiments to determine the effects of sterilization on the sample would then be done and would aid significantly in the reconstruction of the chemical and physical properties of the sample prior to sterilization. Some suggestions are included in the following table.

Pre-return Experiments

The following experiments are important in a general way to assessment of the value of a returned Martian sample.

1. Studies of rates of decomposition of carbonates as a function of temperature and partial pressure of carbon dioxide.

2. Experiments to determine the actual redistribution processes of elements involved in the three different isotopic dating techniques to heating in sterilization environments and in natural environments to temperatures both above and below those required for structural transitions and reactions between phases. This will aid tremendously in the understanding and chronological interpretation of the isotopic systematics obtained on such samples.

3. Some of the minerals and mineral assemblages which are reasonably anticipated as significant Martian rock types have not been adequately studied by all (or any) of the isotopic dating techniques. This must be done to determine the nature of chronological information which can be obtained by each technique and the systematics for obtaining this information. This is particularly true for the $^{40}Ar/^{39}Ar$ technique, which is relatively new and where the proper interpretation of age spectra can be obscure. For this reason, it is recommended that each proposed sample type be thoroughly studied by all dating methods.

4. Careful studies of track annealing as a function of time and temperature.

5. Experiments on relevant minerals to determine the extent of isotopic ratio shifts corresponding to loss, gain, or exchange of structural volatile molecules (e.g. H_2O, CO_2) during sample return and sterilization. For example, comparison of D/H obtained in clays heated in sealed containers to D/H in unheated samples and similar studies for $^{12}C/^{13}C$ from carbonates.

6. Study of the effects of magnetic overprinting by heating for various lengths of time in various environments using fine-grained iron, iron oxides, and iron hydroxides.

APPENDIX I

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APPENDIX II

This appendix contains the correspondence leading to the production of this report, including many of the opinions and data used in forming the conclusions of the report.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
ROOM WASHINGTON, D.C. 20546

FEB 26 9 12 AM '74

REPLY TO
ATTN OF: SL(RSY:dr)

February 21, 1974

Dr. Larry Haskin
Johnson Space Center
Houston, TX 77058

TN
AA, TA

Dear Dr. Haskin:

After our recent conversation on Mars Surface Sample Return missions (MSSR), I am writing to ask you to lend us your expertise and some of your time during this study phase. As you know, we are working very hard to develop a plan for returning Mars samples, which can be presented before our advisory committees, the Space Science Board, and by summer to the Administrator for approval. This is a tight schedule, but we feel it is necessary to get administrative approval to do some serious in depth work on this extremely important mission concept in the next year or two.

You are well aware of the complications in MSSR missions brought about by the concern over back-contamination and the impact of sterilization on the scientific content of the samples and a number of other problems which were discussed at the meeting on this subject held at the Ames Research Center in October. We are currently doing preliminary experimental work on the effects of sterilization of Mars samples on the scientific content of such samples in the inorganic, organic and biological areas. I am hopeful that I can persuade you to play a key role in this endeavor. Work is already going on in several laboratories in the inorganic area (I believe Dr. E. King has brought you up to date). I hope that you will be willing to take the overall responsibility for the inorganic work; to coordinate the work now ongoing, to bring together additional scientific expertise as needed and to provide us with an assessment by April 1. Dick Young has prepared a time-table for reports and reviews and other phases of the work (e.g. Mission analysis, and Quarantine constraints) which you have been sent. In the May-June time frame we plan to develop a final integrated report, to be reviewed by the PSC and the SSB. In this time frame we will also need help in the preparation and presentation of this material and will hope to enlist your further aid.

I think we all agree on the scientific importance of bringing back extraterrestrial samples for study, and of maximizing the scientific

return from such samples. It is only with the help of scientists like yourself that we will be able to do so.

Best regards,

S. I. Rasool
Deputy Director
Planetary Programs
Office of Space Science

cc: G. Wasserburg
S. Dwornik
E. King
R. Young
G. Wetherill

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS 77058

REPLY TO
ATTN OF: TN

MEMORANDUM

TO: Distribution

FROM: TN/Chief, Planetary and Earth Sciences Division

SUBJECT: The Effects of Biological Sterilization on Inorganic Properties of Proposed Returned Martian Sample

NASA is considering the return of material from the Martian surface in the 1980's. Such a sample return is attended with problems of biological quarantine or sterilization. The NASA Administrator has requested some evaluation of the effects of biological sterilization on the inorganic, as opposed to the organic, properties of the Martian material by April 1.

A proper assessment of these effects would require carefully-designed, well-founded experiments and sufficient time in which to do them. The design for these experiments would have to consider a variety of possible simulants based on our best estimates of the compositions of Martian surface materials as well as materials designed to serve as controls for testing other experimental parameters; for example, contamination of the simulant during the sterilization process. The design must carefully establish all protocols for equipment, containers, and handling of the samples under the various conditions of sterilization to be tested.

Some work along these lines has been initiated, with Elbert King serving as the principal representative for inorganic properties (see attached memo). The experiments being done by this group will, no doubt, provide some useful data but because of the time constraint of the April 1 deadline, they are necessarily inadequate in scope and design. We must avoid the danger that those experimental results might be used as a definitive result for a study of the effects of sterilization on inorganic properties. (This problem is well recognized by King and the other participants in the tests.)

We have been asked by NASA's Planetary Programs Office to undertake a somewhat broader evaluation of the problem based principally on existing information. The procedures we will use in order to meet the early deadline are the following: We will discuss the problem of the effects of

sterilization with a variety of experts in fields that bear on the problem. We will gather data and their opinions and obtain the right to reference them. We will also gather, through them, a bibliography of supporting information. Finally, we will select a subgroup of the most knowledgeable and interested experts consulted who represent some range in expertise and who have accepted responsibility for gathering the needed information. This subgroup will gather here with several of us at JSC to discuss the information and to prepare a document giving our present evaluation of the problem.

In order to meet the problem as posed, we shall restrict our efforts to the assessment of the effects of biological sterilization on the inorganic properties of returned Martian materials. Biological protocols have not yet been established or tested. The enclosed documentation offers an assessment of the present state of the efforts of biologists to determine the least severe conditions required to assure adequate sterilization. We shall not, in this study, debate the larger issues of whether a Martian sample should be sterilized or whether, in fact, a Martian sample should be returned. Information bearing on those important questions will, no doubt, result from the considerations required to assess the effects of sterilization. Nevertheless, they must be handled as a separate issue.

In order to structure this study, I list below four questions which I believe will serve as a framework for our analysis.

a. What properties should we measure in returned Martian materials?

b. What is the importance of each of those properties toward understanding the original nature of that material, its development while on the Martian surface, and its inferences for the planetary evolution of Mars?

c. What is the potential effect of sterilization on each of these measurements?

d. What further research is needed in order to provide answers to the previous questions?

For purposes of getting the study underway, I have made an outline of a number of areas of concern that should be considered. In that outline, and as a result of discussions with you and others, I have listed experts in the various fields identified. I request that each of you take responsibility for the area of study in the outline below to which you have been assigned. This includes initial contact with the experts listed below, assistance in drawing together all the information, and assistance in organizing the small gathering to write this document and in helping

produce the finished product. Please note that Pete Toulmin of the U.S. Geological Survey in Washington, who has extensive expertise with the Mars Viking program, has agreed to help us in any way he can.

I. Mineralogy and Petrology (W. Phinney)

A. High Temperature Properties

1. General (D. Wones, J. Papike, E. King, E. Roedder, J. V. Smith)

2. Sublimates, Sulfides (B. Skinner)

3. Microscopic Morphology (D. McKay, J. Schopf)

B. Low Temperature Properties

1. Differential Thermal Analysis Studies (D. Anderson)

2. Carbonate Minerals

3. Clays

4. Limonite, Goethite, Etc.

} H. Eugster, J. Hower, B. Jones

II. Chemical Properties (E. Gibson)

A. Lithophile Elements (R. Schmitt, J. Philpotts, L. Haskin, P. Johnson, R. Taylor)

B. Siderophile, Semi-Volatile Elements (E. Anders, G. Reed, L. Silver)

C. Light, Volatile Elements (E. Gibson, K. Kvenvolden, S. Chang)

D. Surface Properties (D. Cadenhead)

E. Redox Effects (M. Sato)

F. Martian Surface, General (P. Toulmin, H. Holland)

III. Isotopes (L. Nyquist)

A. Noble Gases (D. Heymann, P. Eberhardt, D. Bogard)

B. Stable Light Isotopes (R. Clayton)

C. Ages (G. Wasserburg, B. Doe, M. Tatsumoto)

IV. Physical Properties

A. Tracks (B. Price, C. Naeser)

B. Thermal Luminescence (R. Walker)

C. Magnetics (D. Strangway, M. Fuller)

D. General (R. Housley, O. Anderson)

You should feel free to get assistance from other members of P&ESD as needed both to contribute expertise and to assist you in communicating with the outside experts. Every effort should be made to obtain well-documented opinions from the experts with a minimum of impact on their time. Our final document will not be a definitive assessment of the impact of sterilization on the returned Martian sample; it will merely give our best present estimate and identify areas of research that should be pursued before a definitive assessment can be made.

The list of experts given in the outline and topics given in the outline are, of course, not comprehensive. You should add additional people and topics as necessary for us to develop a proper appraisal of the problem.

Please complete your preliminary survey with these investigators as rapidly as possible. In order to meet the desired schedule, we should discuss our progress on February 25 and have the final inputs from all consulted experts by March 11.

Original Signed By
LARRY A. HASKIN

Larry A. Haskin

5 Enclosures:
1. Letter from E. A. King, Jr.
   to L. A. Haskin, dtd 2/6/74
2. Report on Mars Surface Sample Return
3. Letter from E. A. King, Jr.
   to S. E. Dwornik, dtd 12/27/73
4. Letter from E. A. King, Jr.
   to D. Young, dtd 2/5/74
5. Summary of the Proceedings of the
   Mars Surface Sample Return Symposium

Distribution:
TN6/Dr. W. C. Phinney
TN7/Dr. P. R. Brett
TN7/Dr. E. K. Gibson
TN7/Dr. L. E. Nyquist

cc:
TA/Mr. A. J. Calio
TL/Dr. M. B. Duke
NASA Hqs, Mr. S. E. Dwornik, SL
NASA Hqs, Mr. S. I. Rasool, SL
NASA Hqs, Dr. R. S. Young, SL
Dr. B. R. Doe, U.S.G.S.
Dr. J. W. Head, LSI
Dr. E. A. King, Univ. of Houston
Dr. G. J. Wasserburg, Cal Tech

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS 77058

REPLY TO
ATTN OF: TN7

February 19, 1974

Dear

NASA is presently considering the feasibility of returning material from the Martian surface in the 1980's. Such an exercise again raises the spectre of possible biological contamination of the Earth by harmful organisms. One approach to solving this problem is biological sterilization of the sample prior to its return to Earth. We are soliciting your ideas along with supporting data which might pertain to the problem of how a biological sterilization would affect the useful scientific information available from a Martian sample. The NASA Administrator has requested an initial evaluation of this problem by April 1. Quite simply stated, "What useful information is retained in a sample after biological sterilization?" A proper assessment of these effects will require carefully designed, well founded experiments and sufficient time in which to do them. However, the results of our initial survey must go to the NASA Administrator by April 1.

In order to meet our deadline, we are soliciting the advice and opinions of a variety of experts such as yourself. We wish to obtain data, opinions, and the right to reference them in the report. In addition, we will compile a bibliography of supporting information. The report will be put together at JSC the week following the Fifth Lunar Science Conference.

We are fully aware of different views concerning a returned Martian sample. We shall not, in our study, debate the larger issues of whether a Martian sample should be sterilized to meet the requirements of the biological community or whether, in fact, a Martian sample should be returned. The report that we are preparing will be concerned only with the effects of sterilization on a returned Martian sample. The biological protocols have not yet been established or tested. Several sterilization conditions aboard the returning spacecraft are under consideration, however. They are outlined below:

a. Dry heat sterilization in a container open to interplanetary vacuum.

b. Dry heat sterilized in a sealed container.

c. Heat sterilized in a sealed container with water added to produce 80% relative humidity above the sample.

The times and temperatures under consideration include: (a) 150°C (or lower) for 1 month, (b) 200-250°C for 1 week, (c) 300-350°C for 1 day, and (d) heating to incandescence for a very short time!!!

We need your opinions and data in the following areas:

1. What properties should be measured in a returned Martian sample?

2. What is the importance of each of these properties toward understanding the original nature of that material, its development while on the Martian surface, and its inferences for the planetary evolution of Mars?

3. What is the potential effect of sterilization on each of these measurements?

4. What further research is needed in order to provide answers to the previous questions?

Please note that although we are not concerned with design of the sampling device, the sampling method would influence the nature of the sample returned and, therefore, influence the effects of sterilization on that sample.

We wish to have your written opinions and any supporting data which you might have readily available before March 8. We do not wish to impact your already busy schedule, but whatever information you can supply will be most useful in our report. If you have any colleagues who could provide additional help, please contact them.

Enclosed are two documents giving some supportable guesses on the possible composition of Martian materials. We look forward to hearing your opinions and seeing your data.

Sincerely yours,

2 Enclosures

"Nature of the Martian Surface"

In addition to the enclosed summary of physical, chemical and atmospheric properties at the Martian surface, the following additional information has been gleaned from the literature. References are listed at the end. To consider the arguments and data used for the conclusions listed below, please consult the particular paper cited. In case of conflict between the summary (made in 1968) and more recent data, the more recent data probably are preferable.

1. Properties of the planet.

Mean density = 4 gr/cc (Earth = 5.52 gr/cc) (1).

Magnetic field is less than 0.03 percent that of Earth; no detectable radiation belt exists (1).

2. Surface temperatures and atmospheric pressure.

Maximum T = 25°C, average = -62°C, minimum = -100°C (1).

Total atmospheric pressure 7-20 millibars (1).

Extensive regions where surface pressure exceeds that of triple point of water (2).

Near equatorial surface P = 8.9 mbar (max), 4.95 mbar (mean), 2.8 mbar (mean). At Lat. 65° P = 10.3 mbar (max), 8.9 mbar (mean, 7.2 mbar (min) (3).

3. Atmosphere.

CO_2 >90% (18).

O_2, O_3, CO trace amounts (18).

H_2O ≈5-6 millibars pressure (18).

N_2 upper limit is model dependent (0.5 to 5%) (18).

Ar model dependent (400 ppm to 10%) (18).

5-10 μm precipitable H_2O (1, 19). Wettest conditions (20-30 μm precipitable H_2O) occur over N. polar cap in spring (4).

No evidence of CH_4, NH_3, NO_2, H_2S, formaldehyde, acetaldehyde (1, 19).

Possibly small amounts of ozone present (5).

Spectral measurements sugges $^{12}C/^{13}C$, $^{16}O/^{18}O$ close to terrestrial (2).

4. Composition and particle size at surface.

Spectral analysis of atmospheric dust suggests SiO_2 content of 55 $\pm$ 15% (2) and (17).

Spectral data suggest an abundant mafic silicate (Ca-pyroxene?) component and montmorillonite could be the major component of the Martain dust clouds. Limonite may be a weathering product of the mafic silicates. Limonite does not appear to be a major component, however, a ferric iron component does appear to contribute to the observed spectral reflectivities. A thin Fe^{+3} layer on the particles can account for the color (6 and 17).

An upper limit of approximately 1 wt. % bound water in the surface materials is the probable cause of an observed spectral band (6, 17). However, the major constituents found may be anhydrous (17).

Polar caps receive an annual CO_2 ice deposit on a residual cap of H_2O ice (5).

Ice caps are solid CO_2 (8).

Solid CO_2 is most likely for polar caps, also H_2O ice and CO_2-H_2O clathrate (9).

Nix Olympica is probably basaltic; morphologic evidence suggests

that more differentiated rocks occur elsewhere. Glacio-aeolian layered deposits occur near poles. Isostatic considerations suggest basalt in low flat lands and more differentiated rocks in highlands (10).

Mean particle radius at surface lies between 10 and 300 μm (6).

A current working model envisages a surface composed of unknown proportions of montmorillonite and other clay minerals with fragments of fresh basalt and other more differentiated rock types and fragments of weathered, limonite-stained rocks. In view of the high CO_2 content of the atmosphere the reported low abundance of carbonates (6) is surprising. Areas rich in sublimates doubtless occur, impact breccias and evidence of impact metamorphism should be relatively abundant. An appreciable meteoritic contribution should exist.

5. Surface processes.

Evidence exists for impact, tectonic, volcanic, depositional and erosional activity (including aeolian transport) and fluid formed channels (11).

Fresh impact craters are rare (10).

Evidence of past erosion due to running water (12).

No evidence of pyroclastic deposits (13).

Removal of either ground ice or magma is responsible for so-called chaotic terrain (14).

Large multiringed basins were formed in the same manner as their lunar equivalents (15).

6. Age relations.

Large craters are estimated to be 3-4 by old (16).

Some areologists consider that Nix Olympica erupted as recently as 2-3 my ago.

Additional supporting data as to possible Martian surface materials can be found in the JPL Mars Scientific Model Books available during this meeting. However, these models do not take into account the recent data from Mariner 9.

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18. T. Owen (1974) personal communication.

C-2

3.4 CHEMICAL AND PHYSICAL PROPERTIES

The only data available for the determination of Martian surface composition are spectral reflectance and polarization curves, which suggest a result but often do not uniquely define one. Similarly, there is some indication of the physical condition of large areas of the Martian surface from polarization and thermal conductivity studies implying the presence of fine particles. Information presented in this section has been derived from interpretations of related Martian and lunar observations and from laboratory studies.

DATA SUMMARY

Composition[1]*

Extrapolating from what occurs on the Earth, material components on the Martian surface may include volcanic and extruded material (lava), outgassing sublimates, and meteoritic materials of all types, including dust. The chemical ingredients are virtually the same in all terrestrial lava types but vary considerably in relative proportions. Figure 1 is a tabulation of chemical ingredients in terrestrial lava and crustal rocks and also includes lunar compositional information from the Surveyor alpha-scattering instruments. Outgassing and reaction products that may be present on the Martian surface include carbonates (calcite, magnesite, and dolomite), sulfur, clays, sericite, opal, and talc. The composition and density of the meteoritic flux in the vicinity of Mars have not been measured. Meteoritic minerals found on Earth are given in many standard reference works, e.g., Mason (1962). Observations indicate the possible large-scale presence of basic basaltic-type rock stained and/or mixed with iron oxides (Adams, 1968).

Physical Properties

Particle sizes (<1 mm)	See Fig. 5 (theoretical study based on lunar data)
Size-frequency distribution of particles, fragments, and blocks (≥1 mm)	See Fig. 6 (lunar analog, Surveyor data)
Preferred static bearing strength (lunar analog):	
Up to 1-mm depth	$<0.1 \times 10^5$ dyn cm^{-2} (from imprints of small rolling fragments)
1- to 2-mm depth	0.2×10^5 dyn cm^{-2} (from imprints of alpha-scattering instrument sensor head, Surveyor VII)

*See page 15 for list of cross references.

At about 2-cm depth	1.8×10^5 dyn cm^{-2} (from imprints of crushable block, Surveyors VI and VII)
At 5-cm depth	4.2 to 5.5×10^5 dyn cm^{-2} (from footpad penetration analysis, Surveyor I)

10^5 dyn cm^{-2} =
1 Newton cm^{-2} (N cm^{-2}) (Choate et al., 1968)

Deep deposits of windblown dust having far lower bearing strength could exist in wind shadows.

DISCUSSION

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OF POOR QUALITY

Iron Occurrence

Some models suggest that Mars has not been differentiated to the extent that a nickel-iron core has formed, but rather that it is a fairly homogeneous planet. Since there is still controversy about the nickel-iron-core model of the Earth, this may not represent a substantial argument for the amount of surface differentiation on a planet. It has been suggested that Mars has a lower iron content than Earth, the iron being distributed throughout the planet.[2] Oxides of iron may be common on the surface; however, with the high atmospheric content of CO_2, the stable form of iron on the Martian surface could be siderite, $FeCO_3$ (O'Leary, 1967).[3]

Stability of Terrestrial Iron Oxides

Limonite. The term limonite—from the Greek meaning meadow, in allusion to its occurrence as bog ore in meadows and marshes—applies to a natural hydrated iron oxide mixture, frequently occurring with impurities. Most commonly, a limonite deposit includes the minerals goethite and lepidocrocite as well as iron oxides and hydroxides of undetermined crystallization and hydration.

Goethite. Goethite, $Fe(OH_3)$, is the stable iron oxide under ground-water conditions all over the Earth. Alkaline solutions stabilize goethite and other hydrates. Goethite may form from hydrolysis of silicates and hydration of hematite. In the laboratory a 10% weight loss (of water) is necessary to convert goethite to hematite (Loomis, 1967).

Hematite. Both hematite, Fe_2O_3, and goethite occur naturally in terrestrial soils. However, where hematite coexists with goethite (tropics) it probably is not stable. Hematite may be formed by baking, as a surface product of goethite, but would not rehydrate each time it rains; therefore, hematite would be expected in areas of dry climate with average temperatures of 60 to 70° F. Hematite may also be formed by the weathering of magnetite, Fe_3O_4.

Siderite. Siderite, $FeCO_3$, occurs in large deposits in terrestrial sedimentary rocks. Crystalline specimens are found in sulfide ore veins formed hydrothermally. Siderite is slightly soluble in cold hydrochloric acid.

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Iron Oxides and Silicates on Mars[4]

A large amount of observational data on the geometric albedo of Mars as a function of wavelength has accumulated during the past decade, with excellent agreement among the many workers. These data are summarized in Fig. 2, modified from McCord and Adams (1968). The curve exhibits two major features: a strong broad absorption reaching a minimum below 0.4μ and a shallow broad absorption centered near 1.0μ. In some data there has been a hint of a very weak broad feature near 0.87μ. Such broad features are characteristic of electronic transitions in solids (Adams, 1968).

Early attempts to identify materials responsible for the characteristic Martian spectral reflectance were little more than educated guesses because of the lack of good laboratory comparison spectra of rocks and minerals. Identifications are always complicated by the strong dependence of intensity of the spectral features upon particle size.

The best interpretation today is that the blue absorption is due to ferric ions in the oxide or semi-hydrated form (McCord and Adams, 1968), while the 1μ absorption is due to ferrous ions in a silicate lattice (Adams, 1968). The so-called "limonite band" at 0.87μ is also caused by ferric ions but is not necessarily caused only by that ion as limonite. An excellent match with Martian observations is given by Adams' laboratory curve for an oxidized basalt, shown as the solid line in Fig. 2. Adams' preparation technique involved oxidation with dilute nitric acid, which dissolved some magnetite and resulted in precipitation of ferric oxides and hydroxides as a stain on the rock particles.

A great deal of laboratory work and telescopic observation are still needed to strengthen contemporary theories about the Martian surface. It is unlikely that detailed surface composition can be obtained short of in situ analysis. Nevertheless, there is a reasonable indication, well grounded in observation and laboratory study, that large areas of Mars may be partially composed of materials similar to terrestrial basic basalts stained and/or mixed with iron oxides.

Water and Carbon Dioxide[5]

On the phase diagram (Fig. 3) it can be seen that under prevailing Martian conditions H_2O could occur briefly in the liquid state from 0° to about 5 or 10 C.* The liquid phase, being subject to rapid evaporation, would exist for only short time periods in this restricted temperature range, and the solid phase, if at the surface, would outgas rapidly. Water in either the liquid or solid state would not be detected by spectroscopic methods presently being used. Observed radar data are not inconsistent with water ice which has a dielectric constant of 3.2. Since only a trace of water vapor (in the atmosphere of Mars) has been observed spectroscopically and solid water ice would rapidly outgas, liquid or solid water appear to be possible but improbable surface features.

*Phase diagram relationships are based on pure H_2O and CO_2. Any water on Mars probably would contain dissolved salts and CO_2, this changing the relationship somewhat.

The polar caps are probably mostly solid CO_2 with possibly a core of H_2O ice (Fig. 3). A dark band appears at the edge as the cap begins to recede. This has often been interpreted as melt water, but it seems unlikely that such could really be the case. One of many hypotheses about the nature of the wave of darkening, which moves from the pole to across the equator in Martian spring, is that a melting process of a superficial layer of crystalline H_2O and immediate evaporation or other freeze-thaw phenomena may be indicated.[6] If volcanism is present on Mars, liquid H_2O may exist in adjacent subsurface areas. Any liquid surface H_2O on Mars would contain dissolved CO_2 and thus would become a dilute carbonic acid.

According to a discussion of Martian observations and phase diagram relationships of CO_2 and H_2O (Wade and de Wys, 1968), observed frost phenomena could represent an H_2O sublimate since frost patches have been observed to endure through an entire day and to withstand the accompanying thermal regime.

Mean annual temperatures for all latitudes on Mars are below the freezing point for water, and in polar and subpolar areas theoretical calculations show that temperatures drop below the condensation point for CO_2 during the winters. Small quantities of ice particles could accumulate in cracks which extend below the annual 0° C isotherm and survive. In fact the possibility of perennially frozen ground cannot be ruled out.[7] On the other hand, any CO_2 crystals that settle to such depths will vaporize because of the warmer environment a few centimeters below the surface.

Meteoritic and Magnetic Material[8]

In the Martian areas photographed by Mariner IV, crater density estimates have varied considerably with the counter, depending upon his interpretation of the pictures. The Mariner IV experimenter team has concluded that the most optimistic count results in a crater number density slightly smaller than that of the lunar highlands (Leighton et al., 1967). Sharp (1968) has noted considerable evidence of modification of Martian craters, however, and concludes that erosion or deposition have substantially modified them compared with lunar highlands craters. If impacts are the cause of most Martian craters, an amount of meteoritic debris exceeding that postulated for the Moon may be present (Fig. 4). From Surveyor magnet data (de Wys, 1968) and from that of the alpha-scattering instrument (Turkevich et al., 1968), meteoritic iron addition to the lunar surface material tested appeared to be less than 0.25%. If meteoroid fluxes are 4 to 26 times greater for Mars (Sharp, 1967), there will be a much greater percentage of magnetic material. If this is indeed the case, the surface material will have a higher specific gravity, and this will affect mechanical properties to some extent.

Sizes and Size Distribution of Material

There is no direct information on particle size-frequency distribution curves for Martian surface material. The lunar model may be used as the closest analog (Figs. 5 and 6).

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Polarization, Thermal, and Radar Data [9]

Dollfus and Focas (1966) indicate that an excellent fit to their polarimetric data can be obtained by mixtures of iron oxide particles of all sizes smaller than 200 μ, in which smaller particles envelop the larger ones. A finely pulverized or highly porous surficial layer is also indicated by the thermal parameters. Kachur (1966) suggests that the thermal regime on Mars will produce extensive cracking with accompanying particle-size reduction.

Radar data for Mars indicate a 6 -diameter (planetocentric) area of intense reflection from the planet with a wavelength of 12.5 cm and a 0°.2-diameter area with 40-cm wavelength. This is quite a drop in the size of the area giving intense reflection, a considerably greater area-size change than for the lunar returns. This has been interpreted as due to far more surface roughness on Mars on a scale of 12.5 cm than on a scale of 40 cm. Unfortunately the 40-cm data are very poor.

Mariner IV Data

The resolution is about 3 km on the best of the Mariner IV pictures of the Martian surface; therefore, no direct data are obtained as to the particulate layer. Erosion of crater rims appears to be more active than on lunar crater rims. This suggests more fine-grained material, although if processes are chiefly mass wastage or thermal creep activity, information concerning the fine-grained element is not indicated. A softening of the rim outlines could suggest covering by a fine-grained particulate layer. However, since the resolution is no better than 3 km and a surface haze may have been present (Murray, 1967), this is at best one possibility.

Lunar Data

Lunar surface material at the five widely separated Surveyor landing sites is granular, slightly cohesive, and predominantly fine-grained. Approximately 95% of the soil at the sites is finer than the 1-mm resolution of the television camera. Within the visible size range there is a uniform distribution of particle sizes ranging from the 1-mm camera resolution up to the largest blocks present, which are several meters in diameter. Cumulative size-frequency distribution curves for each Surveyor site are shown in Fig. 6. Figure 7 shows sectors of the lunar surface at the Surveyor I and VII sites. At all Surveyor sites there is a greater percentage of coarse fragments surrounding large craters than occurs on surfaces where large craters are absent. The shapes of the large blocks range from angular to subrounded. Angular blocks mostly rest on the surface with little or no burial, whereas rounded blocks appear to be partly buried.

Bearing Strength

Lunar soil at the five Surveyor landing sites was found to be remarkably similar in bearing strength (Fig. 8) and other physical properties. Based on a Surveyor footpad 30 cm in diameter with a soil penetration of about 5 cm, bearing strength is 1.2 to 5.5 × 10^5 dyn cm^{-2}. Bearing strength based on the much smaller effective surface area (5 cm × 2.5 cm) of the Surveyor III soil

mechanics surface sampler was 2×10^5 dyn cm^{-2} for a soil penetration of 2.5 cm (Scott and Roberson, 1967). The increase of lunar bearing strength with depth as determined from the five Surveyor missions is given on pages 1 and 2.

It is expected that bearing strength of most Martian surfaces will more closely resemble the Moon than the Earth. The great diversity and complexity of Earth's surface materials and their wide range of bearing strengths are not anticipated on Mars. However, it is not expected that the Martian surface will exactly duplicate the Moon. For example, lunar soils were found uniformly to have a small cohesion, the value probably being about 10^4 dyn cm^{-2}. This cohesion is probably associated with the vacuum environment (the lunar atmospheric pressure is estimated to be $\sim 10^{-13}$ Earth atmospheres) or possibly in some cases with sintering caused by energetic particle bombardment.[10] Bearing strength of the top few centimeters of lunar soil is derived mainly from soil cohesion, whereas at progressively greater depths bearing strength is derived mainly from the greater internal friction of the more densely packed soil.

On Mars surface soils may also have cohesion. Such cohesion, however, would probably be caused by water molecules adhering to soil-particle surfaces, not by vacuum sticking, and could therefore vary as the abundance of water varied—both with place and time on the Martian surface.[10]

The bearing strength of Martian soils with cohesion could be assumed conservatively to be the same as lunar soils. For Martian soils that are essentially cohesionless, an Earth analog of soils found in active dune sands and fine ash deposits around geologically recent volcanoes can be used. For loose soils with very low cohesion, surface bearing strength varies with grain size because coarse-grained soils (i.e., sand-sized) assume denser packing at the surface during deposition than do fine-grained soils (i.e., silt-sized). Examples of fine, loosely packed surface soils with low bearing strength are the ash deposits on the flats surrounding Cinder Cone in the Lassen Volcanic field and the ash field west of the 8443-ft peak at Mono Craters in California. The yellow clouds of Mars[11] and the polarization data indicate the probable existence of considerable material of very small particle size, a great deal of it smaller than 200 μ, much of it smaller than 50 μ. Collections of such fine dust in completely dry sites could prove quite hazardous to landing machinery, particularly on inclines or in dunes with surfaces approaching the angle of repose (34°).

CONCLUSIONS

1) A finely divided particulate surface layer appears to be indicated, with little composition difference between light and dark areas. Iron oxides are probably common, perhaps as a desert-varnish-type coating on silicate grains. Basaltic-type material is probably common, perhaps as lava flows as well as small grains.

2) Size-frequency distribution curves for volcanic debris and impact debris may serve as upper and lower extremes for the Martian surface material.

3) At present the lunar bearing strength data may be considered as a best estimate for the Martian surface. Deep, soft deposits of windblown dust, however, could exist in wind shadows.

4) Many investigators hypothesize a greater meteoroidal flux at Mars than at the Moon, although there is little agreement on the magnitude of the difference. There is no direct evidence of flux differences, as the age and origin of Martian craters are not firmly established.

5) The polar caps are probably mostly CO_2 ice with a possible core of H_2O ice.

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Element	Terrestrial crustal rocks,[a] weight % (Holmes, 1965)	Lunar surface material,[b] atomic % (Turkevich et al., 1968)			
		Mare Tranquillitatis: Surveyor V		Sinus Medii: Surveyor VI	Tycho area: Surveyor VII, sample 1
		Sample 1	Sample 2		
Carbon, C		<3	<3	<2	<2
Oxygen, O	46.60	58 ±5	56 ±5	57 ±5	58 ±5
Silicon, Si	27.72	18.5 ±3	19 ±3	22 ±4	18 ±4
Aluminum, Al	8.13	6.5 ±2	6.5 ±2	6.5 ±2	9 ±3[d]
Iron, "Fe"[c]	5.00	13 ±3[g]	13 ±3[g]	5 ±2	2 ±1
Calcium, "Ca"[f]	3.63			6 ±2	6 ±2
Magnesium, Mg	2.09	3 ±3	3 ±3	3 ±3	4 ±3
Sodium, Na[h]	2.83	<2	<2	<2	<3
Potassium, K	2.59				
Titanium, Ti	0.44				
Hydrogen, H	0.14				
Phosphorous, P	0.12				
	99.29				

Oxide	Terrestrial lavas, weight % (Bullard, 1962)			Terrestrial crustal rocks,[a] weight % (Holmes, 1965)	Lunar surface material,[c] weight % (Turkevich et al., 1968)	
	Acid lava	Intermediate lava	Basaltic lava		Mare sites: Surveyors V and VI	Highland site: Surveyor VII
Silica, SiO_2	≥70	59	<49	59.26	50	50
Alumina, Al_2O_3	12-15	16	16	15.35	14[d]	21
Iron oxides Fe_2O_3	≤3	7	12	3.14	16	7
Iron oxides FeO				3.74		
Lime, CaO		6	9	5.08	15	15
Magnesia, MgO		3	6	3.46	5	7
Soda, Na_2O (alkali)	6-8	4	<3	3.81	—[h]	—[h]
Potash, K_2O (alkali)		2		3.12		
Titania, TiO_2				0.73		
Water, H_2O				1.26		
Phosphorous pentoxide, P_2O_5				0.28		
				99.23		

[a] Average composition.

[b] Preliminary analytical results of each alpha-scattering experiment. (The alpha-scattering method of chemical analysis can provide quantitative information on all major elements in a sample except hydrogen, helium, and lithium.)

[c] Consistent with preliminary analytical results of each alpha-scattering experiment. (These data were inferred from elemental results; the alpha-scattering instruments were not designed to provide direct information about the chemical state of the elements measured.)

[d] The value for aluminum for sample 1 on Surveyor VII has previously been reported as 6 ±3%; additional data analysis indicates 9 ±3% is more nearly correct. The Al_2O_3 value for the mare sites is slightly higher than that (13%) reported earlier by the experimenters. The difference arises from rounding-off errors in the earlier analyses.

[e] For lunar surface material, "Fe" here denotes elements with mass numbers between approximately 47 and 65 and includes, for example, Cr, Fe, and Ni.

[f] For lunar surface material, "Ca" here denotes elements with mass numbers between approximately 30 and 47 and includes, for example, P, S, K, and Ca.

[g] The Surveyor V "Fe" and "Ca" groups have not yet been resolved; however, a lower limit of 3% of "Fe" can be set for each of the samples.

[h] The presence of Na in lunar surface material has not been established with certainty. Na_2O could be present in amounts up to 3% by weight in the mare samples and 4% in the highland samples.

Fig. 1. Table of general chemical ingredients in terrestrial lavas and crustal rocks, and Surveyor lunar compositional data.

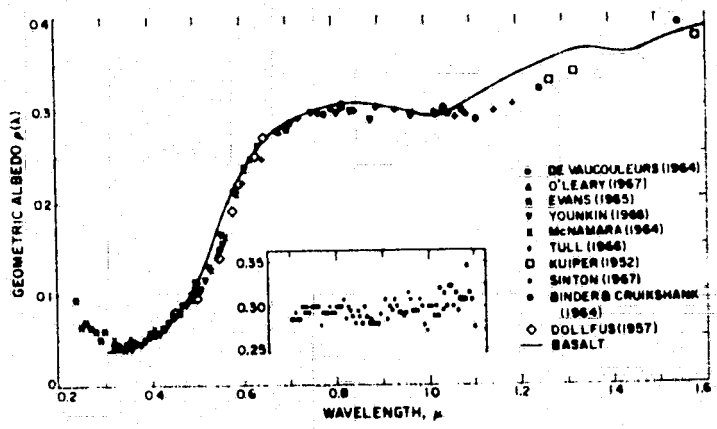


Fig. 2. Comparison of the geometric albedo of Mars (adapted from McCord and Adams, 1968) with the reflectance of an oxidized basalt (Adams, 1968). The basalt measurement was made on an integrating sphere. The specimen, a powder finer than 100 μ, consisted of 50% Little Lake basalt and 50% Boulder County basalt. Oxidation was by treatment in dilute HNO_3, which partially dissolves and oxidizes small grains of magnetite.

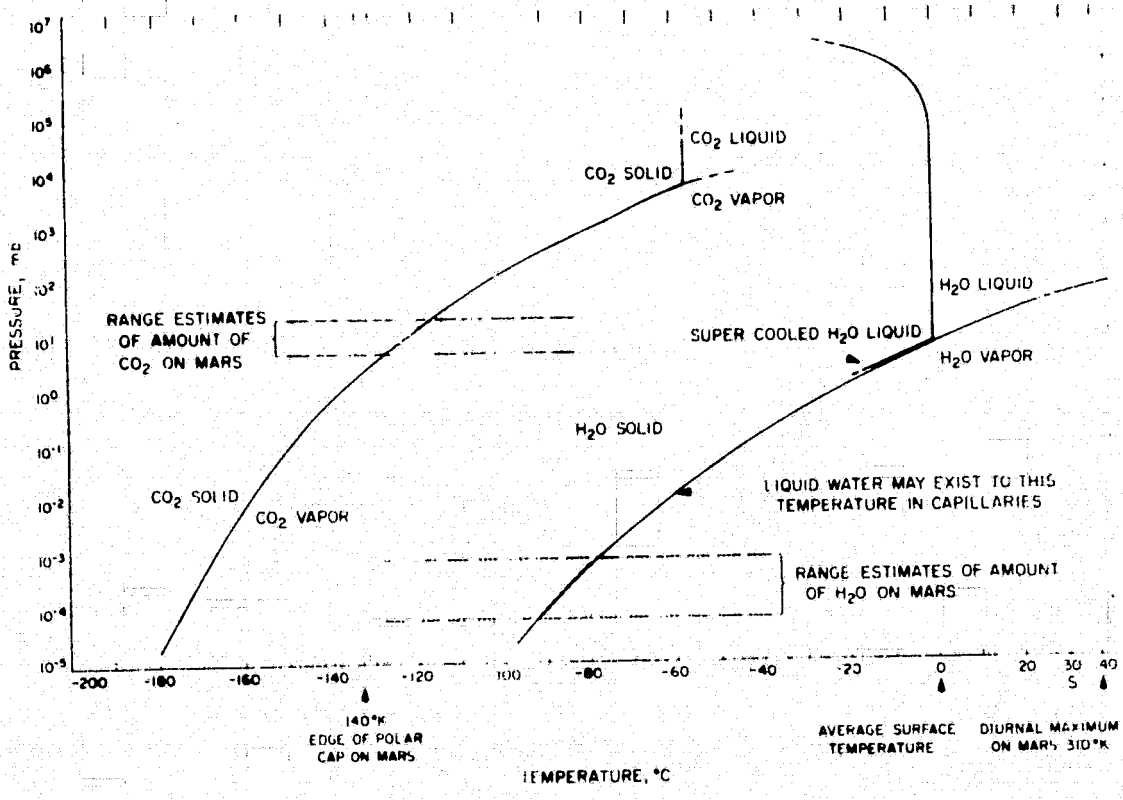


Fig. 3. Phase diagram for carbon dioxide and water. Linear-log plot. (Wade and de Wys, 1968)

DEPARTMENT OF THE ARMY
U.S. ARMY COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE 03755

CRREL-RE

11 March 1974

Mr. W. C. Phinney
National Aeronautics &
Space Administration
Lyndon B. Johnson Space Center
Houston, TX 77058

Dear Bill:

In answer to your questions regarding the effects of sterilization on a returned Martian sample, I restrict myself to those aspects bearing on water relationships. A determination of water in the Martian regolith is an important goal of planetary exploration. It is desirable to extract as much information bearing on this question as possible. Ices, frost and other forms of free water likely will be lost or the measurement compromised during sample acquisition and sterilization; combined forms, however, may be preserved if sterilization is skillfully done. Therefore, an analysis of the returned sample for clay minerals and mineral hydrates should be a goal. The clay mineral and mineral hydrate suites revealed in such an analysis would give important clues as to the water regimes experienced earlier by the planet and that now prevail. Too high temperatures during sterilization could cause irreversible water loss, clay lattice collapse and mineral decomposition that would complicate the analysis or render the analysis useless. Temperatures above 200°C are highly undesirable. Chemical sterilization should be considered and the exposure to lethal radiation levels is also an option to be explored. I inclose weight loss (water loss) data illustrative of the problem. It is found on the pages marked and turned down in the inclosed viewgraph package prepared for the planetary soil water analyzer instrument.

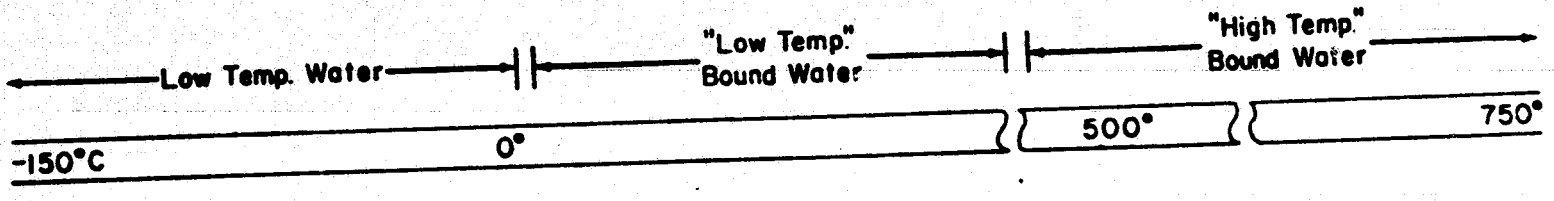
Sincerely yours,

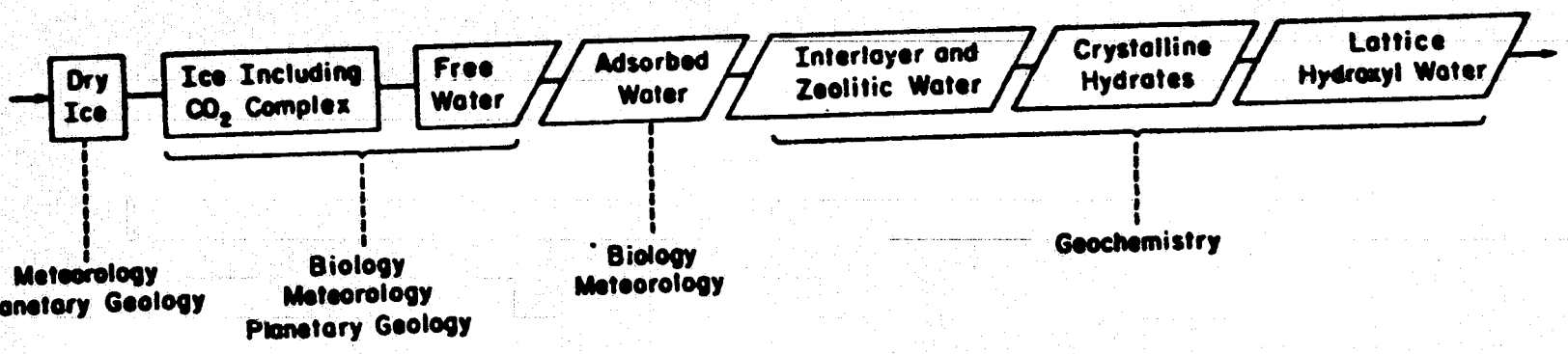
for DUWAYNE M. ANDERSON
Chief, Earth Sciences Branch

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as stated

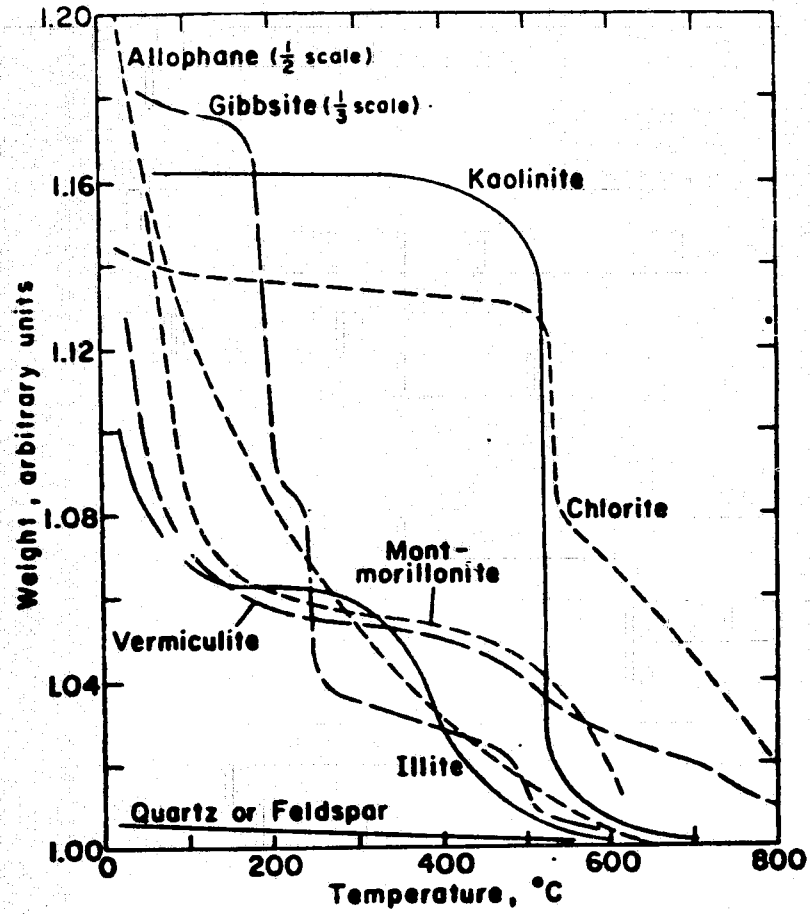
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CATEGORIES OF SOIL WATER EXPECTED ON MARS





DEHYDRATION DATA FOR REPRESENTATIVE MINERALS*



*After Grimm, 1968

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF EARTH SCIENCES

January 8, 1974

Dr. Stephen Dwornik
Chief, Planetary Programs
Code SL
NASA Headquarters
Washington, D.C. 20546

Dear Steve:

Following is a brief discussion of what we think should be done with Martian samples and what environmental constraints need to be placed on returning, de-contaminating, and handling them. This is written from the point of view of our laboratory only. A more general discussion of other types of measurements that should be made by other laboratories would, of course, add additional constraints. We would be glad to extend any part of the discussion should the need arise.

(1) Delineation of dynamic processes in the Martian environment: This can be examined by cosmic ray particle tracks, rare gas records, and by measurements of thermoluminescence in samples of soil and rock. In addition, observations of rock morphology and surface features (wind abrasion pits and striations, etc.) can help delineate processes modifying the Martian surface.

Cosmic rays easily penetrate the current tenuous atmosphere of Mars producing characteristic effects in surface materials. Both heavy particle tracks and spallation-produced isotopes could be studied to give information about sample surface exposure times and erosion rates. In contrast to lunar samples, solar flare particles would be attenuated by the atmosphere, but there should be no problem with galactic cosmic ray effects.

If a stratified sample of Martian soil could be collected, it would be possible to study the variation in total atmospheric pressure with time. This can be done since additional shielding affects the heavy particles that are responsible for track production much more rapidly than the protons. ~~that~~ Shielding would produce a greatly reduced ratio of tracks to spallation products and would also give a characteristic change in the fossil track spectrum.

The amount of thermoluminescence stored in a lunar soil sample depends on its depth below the lunar surface. At the very surface, the TL drains due to surface heating but at greater depths, where the temperature fluctuations are less, the TL first rises and then decreases again. This final decrease is due to an absorption of the cosmic rays originally

responsible for the effect. TL studies in lunar samples have proven useful in establishing the depth of certain samples (e.g., half-filled core tubes) and might give important information on Mars concerning the surface motion of materials. We are also attempting to use TL measurements to establish the temperature gradient in the lunar surface, i.e., measure the lunar heat flow. If this is shown to be feasible, it would be an extremely important measurement to make on a Martian core sample.

(2) Evolution of the atmosphere and crust: For samples of any age, rare gas mass spectrometry can be used to determine ages by the ^{39}Ar-^{40}Ar method. This work, which can be done on individual fragments as small as 10 mg, would serve to establish the basic chronology of the planet. Even a simple scoop sample containing numerous small fragments would yield crucial information.

If some of the samples turned out to be extremely old ($\gtrsim 3.9 \times 10^9$ y), the detailed study of extinct isotope effects (^{244}Pu and ^{129}I), which is a speciality of our laboratory, would give a fine scale chronology for the early evolution of the planet.

The study of trapped gases by mass spectrometry might be an extremely fruitful way to investigate the evolution of the planet. Collection and study of an atmospheric sample in concert with gases adsorbed on rock and soil samples would be desireable. Heavy gases such as krypton and xenon may reside primarily on surfaces rather than being free in the atmosphere.

Petrologic and geochemical investigations of rock and soil samples would clearly be an important phase. A formidable amount of information could be obtained from petrologic study of polished thin sections made from Martian rocks. The most obvious observation would be the identification of the major lithologies present in the vicinity of the landing site. Further, since Martian winds may distribute small rock fragments over large areas of the planet's surface, a scoop of soil obtained in one locality might contain samples of rocks that do not outcrop near the landing site. If basaltic rocks are present, as seems likely, inferences may be drawn about the composition of the magmas, their oxygen fugacities, and their pre-and post-eruption crystallization histories from electron microprobe measurements of the compositions of the minerals present. Finally, study of the weathering products of the minerals in Martian rocks would set constraints on the composition of the atmosphere, thereby supplementing direct measurements, and it might also yield data concerning long-term climatic variations.

(3) Sample gathering: Although a simple scoop sample would give much information, it is clear that more information would be obtained from our various measurements with more sophisticated sampling techniques - roving ability, the ability to chip boulders, etc. Perhaps the most important of sampling consideration would be the ability to take a vertical core which might provide a layered structure with a definable chronology.

(4) Handling and sterilization constraints: We now consider the constraints our experimental requirements impose on the sterilization of the samples. These constraints are threefold: exposure to organic materials, exposure to heat, and exposure to light or to penetrating radiations such as x-rays and γ-rays.

The thermoluminescence work imposes the severest constraints. The samples should not be heated above 100°C or exposed to penetrating radiations. Even exposure to visible light degrades the results and sampling is ideally performed in red light.

Tracks anneal out in different materials at different temperatures. In feldspars and pyroxenes, tracks anneal out in approximately 1 hr at 550°C; however, in glasses they may anneal out in hrs at room temperature or at 500°C depending on the composition of the glass. Extended exposure to temperatures in excess of 300°C would likely wipe out the track work (literally!), but even lower temperatures might severely degrade the information available.

The rare gas work is also constrained by temperature and exposures above room temperature which would degrade the information obtainable. Exposure to organic molecules should be rigorously avoided. Clearly, exposure to the terrestrial atmosphere should be avoided.

The mineralogy and petrology of igneous rocks could be affected by temperatures of a few hundred degrees, depending on the duration of the heating. However, some lunar breccias have textures showing they have never been exposed to temperatures >300°C. Martian analogs of the latter type rocks would therefore be degraded by temperatures >300°C. In contrast to lunar rocks, Martian rocks may have hydrated minerals that could be affected at temperatures as low as 150°C.

(5) Proposed scenario for sample handling: The summary message contained in the last section is simple: Almost any treatment of the samples will result in a degradation of the scientific information contained in them. The problem of sterilization should probably be re-phrased as follows: "What tests can be performed on a portion of any returned sample to ensure that the remainder of the sample can be examined in a pristine condition."

We propose the following scenario for sample handling: (1) gather atmospheric, soil, and rock samples and seal them in light-tight vacuum chambers; (2) return them to an earth-orbiting space station where they can be examined and small portions can be exposed to biological examination; (3) if the results are negative, then the remaining material could be returned to earth. If they are positive, then a portion of the material could be sterilized with an unfortunate, but potentially necessary, sacrifice of information. Some experiments, as for example the track studies and the initial mineralogical and petrographical studies, could be performed directly in an orbiting space station by trained observers using a minimum of equipment.

Both faculty from the Laboratory of Space Physics (C.M. Hohenberg; R.M. Walker) and the Department of Earth Sciences (R.E. Arvidson; G. Crozaz; F.A. Podosek; G.J. Taylor) have contributed to this discussion. Please note that all proposed observations and measurements on a Martian sample could be done at Washington University and all of them have already been applied here to lunar samples.

Cordially,

REA/mb

Raymond E. Arvidson

UNIVERSITY OF WISCONSIN
Department of Geology and Geophysics
Science Hall
Madison, Wisconsin 53706
Telephone 608 262-2360

February 26, 1974

Dr. W. C. Phinney
N.A.S.A.--Geology
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill,

This letter is in response to your query of February 19 regarding the possible effects of biological sterilization on clay samples returned from Mars.

The following reactions of clay minerals to temperature are relevant.

1. Clays with surface OH groups, such as kaolins, serpentines, and corresponding Fe-compositions start to dehydroxylate around 350°C. The dehydrated phase is X-ray amorphous, and cannot be reconstituted. Temperatures above 350°C, therefore, preclude identification and scientific study of such clays.

2. Clays with 2:1 type layers and H_2O present in the interlayer space will lose their interlayer water as low as 75°-100° C, but do not become amorphous until about 500° to 600°C. For smectite clays (= montmorillonite group) this dehydration is reversible as long as a temperature of 200°-300°C (depending on composition) is not exceeded. Above this temperature the characteristic reversibility of hydration and solvation with organic liquids cannot be studied.

3. Other clay minerals are slightly more tolerant to temperature, but structural changes can be expected in chlorite, sepiolite, and palygorskite above 400°C.

4. Terrestrial smectites sometimes contain organic material in the interlayer space. Indeed, one theory of the origin of life holds that early life forms used the hexagonal clay structure as a template and were shielded in the interlayer space of smectites from an hostile environment. I cannot advise you as to what temperature might change such interlayer material.

Recommendations:

1. 250°C is the maximum permissable temperature, but 150°C would be much safer in view of the unknown types and compositions of Martian clays.

2. A sealed container with 80% relative humidity would appear best for clays, but only if ferrous iron is absent. Distilled water is essential.

Sincerely yours,

Bailey

SWB:ab

S. W. Bailey

State University of New York at Buffalo

OFFICE OF THE CHAIRMAN
Department of Chemistry

FACULTY OF NATURAL SCIENCES AND MATHEMATICS

March 1, 1974

Dr. E. K. Gibson, Jr.
National Aeronautics and
Space Adminstration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Gibson:

Enclosed are my comments on the types of experiments we could complete on possible Martian returns following sterilization procedures. The only thing I seemed to have missed from the list is that we prefer long heating times and low temperatures to short heating times and high temperatures.

Yours sincerely,

D. A. Cadenhead
Associate Professor

DAC:ms

Properties to be Measured

1. Gas content and nature on sample outgassing
2. Surface area and (helium) soil specific gravity
3. Soil density and porosity.
4. Gas interactions (physical and chemical) with sample surfaces.

Temperature Conditions

1. Heating to incandescence would mean an almost total loss of all the information which we gather or may be deduced from our studies: nature and amount of gases evolved, surface areas, soil particle specific gravities, soil densities. The outgassing, sintering, changes in the chemical nature of the surface would render our measurements virtually meaningless.

2. As part of our initial preparation of lunar samples for gas interaction studies we have generally outgassed at approximately 150°C assuming this to be a maximum equatorial lunar temperature. In a similar fashion 25°C would certainly be a safe heat treatment temperature for Martian soil, indeed unless Martian materials are substantially different from Lunar materials 150°C would probably have little or no affect on our measurements at least in vacuum. We would expect significant effects to occur as the preheating temperature is raised from 200 to 350°C.

Vacuum Conditions

Obviously exposure to the vacuum of space would result in a substantial loss of information on gas content especially if accompanied by heating. Nevertheless, from the point of the bulk of our measurements we would prefer the use of ultra-high vacuum conditions to high temperatures.

Heat Treatment in a Sealed Container

Simple heat treatment in a sealed container (sample in its own atmosphere) could and would result in sample surface chemical changes accompanyed by a change in both the pressure and nature of the gases present due to catalytic action. Typically, such processes could give rise to a variety of organic molecules or even amino acid precursers depending on the initial gas composition.

We would consider autoclaving with water vapor even more serious since all of our experiments (with lunar materials) indicate that exposure to water vapor at high temperatures can significantly affect surface area and pore structure measurements in addition to possible effects listed above.

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Astrogeologic Studies
345 Middlefield Road
Menlo Park, California
94025

March 5, 1974

Dr. Robin Brett
Code TN-6
NASA Johnson Spacecraft Center
Houston, Texas 77058

Dear Robin:

Enclosed is a very quick write-up on returned Mars samples. I don't like it but it really is all I have time for right now. Sorry I could not put in time and give you something decent.

Yours sincerely,

Mike

Michael H. Carr

CC: Masursky

Returned Mars Samples

The analysis of returned lunar samples has completely transformed our concepts of how the Moon formed and what its subsequent history has been. Our present knowledge of the timing of events that led to the Moon's present configuration, the differentiation sequence, the bulk and trace element geochemistry and how it differs from that of the Earth have all been derived from examination of returned samples. The degree to which this understanding could have been achieved solely by remote analysis is a matter of conjecture but here is ample reason to be skeptical. Having lunar samples in hand allowed the complete analytical and intellectual capability of the scientific community to focus on the problem of the Moon's origin. Instead of having a small pre-determined set of analytical techniques applied to the samples, the approach could be both all-encompassing and flexible, the analytical emphasis shifting as the meaning of each set of results become better appreciated. There is no reason to believe that these enormous advantages of returned samples should be any less for Mars. Indeed the apparently more complex geology of Mars enhances the importance of the kind of comprehensive examination that a returned sample allows.

This is not to demean the value of remote analysis. In situ analysis are an essential prelude. Before returning a sample to Earth, selection criteria must be established. We should have some understanding of the degree of crustal differentiation and the extent to which surface materials are fractionated by processes such as aeolian or fluvial action. Only then can we ensure against returning to Earth only fractionated extremes such as a pure quartz sand or an evaporite.

The surface of Mars appears to be markedly heterogeneous, one hemisphere being largely primitive cratered terrain and the other being of later materials. Volcanic and tectonic activity appears to have occurred throughout the planets history, probably up to the present day. Despite the inability of liquid water to exist at the surface, there is abundant evidence of fluvial erosion, seemingly by liquid water, suggesting different past climatic conditions. At the poles, layered deposits may contain a record of past conditions as well as being a repository of volatile compounds. These present concepts, largely established by the Mariner 9 mission, cause the following basic questions to be posed:

1. What is the bulk chemistry of the planet and how does it differ from the Earth, the Moon and meteorites?

2. To what extent is the planet differentiated into separate layers and what is the nature of the layers and the histroy of their formation?

3. Does the hemispheric division of the crust result from a primitive segregation or later erosional and volcanic events?

4. What is the timing and nature of different volcanic and tectonic episodes and how are they correlated with the outgassing history?

5. What is the outgassing history of the planet and the subsequent fate of volatiles on the surface?

An understanding of the fate of volatiles on the surface will immediately result from a returned sample. The efficacy of weathering on Mars is largely unknown. It has been argued that the lack of water to dissolve and remove weathered products results in the formation of a diffusion barrier which prevents further weathering. However, the ability of aeolian processes or adsorbed water to remove weathering products is

poorly understood and weathering could be relatively efficient, resulting in large amounts of volatiles being tied up in weathered products. The detailed mineralogy of returned samples will reveal immediately the extent to which weathering has occurred and what the volatiles involved were. Once a weathering model has been established then a meaningful inventory of near surface volatiles can be made. Ages on weathered and unweathered products will allow estimates of rates of accumulation on volatiles in weathered products and place constraints on outgassing models. The chemistry of the volatiles themselves, by comparison with the Earth and the Moon will provide insights into the fractionation history of the planet and the primitive solar nebula.

If the large Martian channels are formed by water then evaporite deposits may occur at their mouths. The lack of evaporite would indicate the channels formed by floods of water that have been in contact with the surface for periods of time that are short compared with weathering rates. The presence of carbonates, sulphates and other evaporite minerals would inidcate long periods of run off and evaporation, or residence times for subsurface waters that are long enough to have allowed solution on a large scale.

The interrelation of volcanic activity and outgassing is unclear and of prime importance in understanding the history of present surface. Two general models of outgassing are held. One assumes an early volcanic period with intense outgassing and relatively little subsequent emission of volatiles in later volcanics are relatively volatile poor. The other assumes steady emission of volatiles throughout the planets history. Returned samples would readily resolve the differences.

A wide variety of volcanic features occur on the Mars surface. The extent to which these result from compositional differences is not known but the wide range of morphologic types must surely indicate that chemical differences do exist, both areally and as a function of age. Documentation of the chemical and petrologic characteristics of different types of volcanic rocks and the dating of different volcanic events will lead to an understanding of the variety of Martian volcanic processes and how they differ from those on the Earth and the Moon. More importantly the knowledge will place tight constraints on thermal and compositional models of the interior. Of particular importance here are details of phase reactions which would indicate the chemical and physical environment at depths, trace element geochemistry, which would give clues concerning fractionation processes, and the different types of age dates. All these almost certainly require a returned sample. Recent modelling suggests high iron contents in the mantle and peaking of volcanic activity in recent past, but constraints on such models are presently very loose. Returned samples will enable these models to be refined so that they can be used in comparison with the Earth and the Moon to arrive at general models for the evolution of planetary interiors.

The question of whether the crust is differentiated into components analogous to the sial and sima of the Earth is of extreme importance in understanding the early history of Mars and the Earth. The separation of continental masses on the Earth had already been achieved 3.8 b.y. ago, but apparently never occurred on the Moon. The mechanism whereby this was achieved on the Earth, whether it required plate motion, or intensive weathering, is unclear. If Mars represents an intermediate

stage, with the two hemispheres being compositionally distinct, then this would provide some insight into how crustal differentiation was accomplished on the Earth. Returned samples will certainly reveal whether the different morphologies of the two hemispheres reflect fundamental compositional differences and whether they are similar to those found on Earth. Detailed chemistry and dates will give clues as to the particuliar mechanism.

One of the most striking results of the lunar sample return program was the unexpected bulk composition of the Moon. The bulk composition of Mars is of even more significance in that it will be the first time we have sampled in another part of the solar system. We will then be in a position to address some fundamental questions concerning the evolution of the solar system such as what was the nature of any chemical inhomogeneities in the solar nebula just prior to accretion, what were the physical conditions which gave rise to the inhomogeneities and did the final accretion give rise to the present array of bodies or an array that was subsequently altered. Unfortunately, bulk composition cannot be directly measured. Its evaluation requires very detailed and subtle knowledge of the chemical balance within the planet. To achieve this, we must have a general understanding of all the processes that have caused chemical change within the planet and the history of their action. Such an understanding can be realized with the kind of comprehensive analytical approach that a returned sample allows.

TYPED COPY OF HANDWRITTEN LETTER

TO: Larry Nyquist

SUBJECT: Sterilization Procedure for Mars Mission and Radioactive Isotopes

The production of radioactive tritium (12.6g) and ^{14}C (5700g) by galactic cosmic radiation in the Mars atmosphere and surface materials could be of great importance in understanding geochemical processes on Mars. An initial determination of the specific activities of tritium in water, and ^{14}C in carbon dioxide, carbonates, and possible organic compounds should be measured on returned materials. These compounds would be in the vapor phase if the sample were in a sealed container. Provisions should be made for removing the gas (via a puncture seal) from the container to measure these activities and make other studies. I can conceive numerous biological and chemical observations that should be made on these gases.

My first thoughts are that the activity determinations would not be severely affected by a mild sterilization if that is deemed necessary. Of the options given in Dr. Clark's letter of February 19, I would strongly favor dry heat sterilization in a sealed container at minimum temperatures, say 150°C for a month.

Sincerely yours,

(Original signed by Raymond Davis, Jr.)

Raymond Davis, Jr.
Brookhaven National Laboratory
Upton, New York 11973

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO

Branch of Isotope Geology

February 20, 1974

Mr. Larry A. Haskin
Code TN
Planetary and Earth Sciences Division
NASA, Johnson Space Center
Houston, Texas 77058

Dear Larry:

Naturally, I am flattered to receive the various documents regarding a possible sample return from Mars in the 1980's and to have my advice solicited. In the time period available for reply, I fear I cannot give the matter very penetrative thought. My duties the rest of this fiscal year as Vice-Chairman of LSAPT provide me with more action than I can handle in a satisfactory manner, and next fiscal year I will be participating in a minerals program. However, I will furnish you with my best "top of the head" thoughts, which seem to be what is called for at this time.

(1) There are three prime dating techniques that should be pursued:

(a) K-Ar (and $^{40}Ar/^{39}Ar$) method which can also be coupled with rare gas studies (extinct ^{244}Pu, etc.).

(b) Rb-Sr method, which has proven so useful in dating the time of formation of unmetamorphosed rocks or the age of metamorphism on metamorphosed rocks. If Martian rocks returned are "granitic," both rock formation and metamorphic ages might be determined by use of whole-rock and mineral isochrons.

(c) U-Th-Pb method, which also involves two refractory elements (U and Th) as well as one of the best "volatile" metallic elements, Pb. This method offers certain advantages arising from an essentially constant ratio of $^{238}U/^{235}U$ in nature, so far as we know, in permitting a direct solution to two-stage effects. Should

all complicating effects on the ratio of radioactive parent to radiogenic daughter occur only very recently, the U-Pb system is the only one not dependent of the observed value of U/Pb.

(2) The effects of the candidate sterilization procedures on the above techniques will require extensive research work, and I recommend a one-year contract be let on each of the above dating methods to determine the possible effects of the candidate sterilization procedure on the most likely rock types.

(a) If the returned sample is rich in clays, argon may be lost in all heating methods.

(b) We do not know what effects water or CO_2 may introduce to the Rb-Sr and U-Th-Pb systems in the Martian sample case, particularly in destroying internal isochrons, although little effect seems to have occurred to the anhydrous lunar *rocks* (soils are a different matter) under lunar ambient conditions of temperature and vacuum. We do know that about 10 percent of the lead can be volatilized from lunar samples in vacuum heated to 500°C for a few hours.

(3) I am most attracted at this stage to sterilization in a sealed container at the lowest possible temperature, even if for the longest time. However, the Rb-Sr and U-Th-Pb systems on anhydrous *rocks* (not soils) might be least affected, if heated to incandescence for an "instant" at 1 atm of nitrogen. The sealed container would be important to trap released condensibles to judge what actually happened. I hope that other radiative non-thermal sterilization procedures will be investigated (radar waves or some such). I am surprised that cosmic ray exposure for several months during return is not judged sufficient, in fact. Experimentation will be required, and testing effects of sterilization on internal isochrons is a big job.

(4) I would hope that in addition to sterilization protocols, display and political privilege protocols would also be worked out well in advance. I recommend that no more than 10 percent of the returned Martian samples be used for such purposes. In view of the small size of the sample return, three displays would appear to be suitable: a stationary display at the National Museum of Natural History, a traveling display devoted to touring the U. S., and a traveling display to tour UN countries. I feel it is important to prevent the types of dubious practices being applied to lunar samples from recurring on the smaller return of Martian samples.

Sincerely,

Bruce R. Doe

Copies to: Larry Nyquist
Everett Gibson
M. Tatsumoto
G. J. Wasserburg

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF GEOLOGICAL
AND PLANETARY SCIENCES

TELEPHONE (213) 795-6811

March 11, 1974
RE: TN7

Everett K. Gibson, Jr.
National Aeronautics and Space
Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett,

In response to your letter requesting my opinions regarding the nature of research that could be done on Martian samples in the light of the various degrees of sterilization that they will undergo, I am assuming that you are primarily interested in the sort of work in which I have some expertise. Otherwise if I were to respond to your questions regarding all scientific work that could be done, I am sure that I, like many other of my colleagues, would probably have to write a textbook. On that premise I will make the following comments.

I would consider Mars a stable isotope planet in that like the Earth it should be subject to enormous isotopic fractionation due to a large number of processes of evaporation, low temperature reactions, long term isotopic exchange between the CO_2, H_2O and rocks, and a host of other very important parameters. The isotopic abundances would therefore give very interesting information, making the study of processes of Mars isotopically somewhat similar to the uses of isotopes that can be made on the surface of the Earth's materials. In this sense I believe Mars would be a fascinating planet to investigate isotopically.

(a) Dry heat sterilization in a container open to interplanetary vacuum.

Naturally the less heating and the shorter the time of heating the sample suffers the more desirable would be the sample. Any kind of exposure of the sample to interplanetary vacuum introduces the peril of loss of many volatiles including CO_2, water, CO, H_2, etc., which for my part would be most unfortunate because I believe that the volatiles on Mars could give us an enormous amount of information regarding surface conditions of Mars as well as the history of escape of water and CO_2 from the Martian atmosphere and the nature and perhaps the mechanisms of introduction of these volatiles to the atmosphere of Mars. The isotopic abundances of hydrogen, carbon, and oxygen would be most valuable for these volatile materials. On the other hand as far as the nonvolatile materials like the silicates and other crystallized materials are concerned, low temperature (150°C) sterilization in vacuum would probably not destroy the isotopic equilibrium relationships between the various minerals in which there could be a record of both low and high temperature processes. Under all circumstances there would always be some materials which would be useful for stable isotope analysis irrespective of the degree of loss in interplanetary vacuum provided that the loss is not complete.

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(b) Dry heat sterilization in sealed vacuum.

Aside from the choice of bringing back pristine samples from Mars, the driest heat sterilization in a sealed vacuum probably appeals to me most. It would probably preserve much of the gases as well as other volatile materials and, if this sterilization is carried out at reasonably low temperatures, there would be a great deal of samples with their integrity preserved. Again I opt for the low temperature, long period of time rather than heating to incandescence over a very short time. It might be possible, if high temperature is avoided, to measure equilibrium partition between various phases and many of the rare gases that there would be in these samples. This information would be most valuable for understanding the history of Martian rocks.

(c) Heating sterilization in a sealed container with water added to produce 80% relative humidity.

This method of sterilization is almost on a par with heating it in vacuum. Water is an excellent catalyst facilitating oxygen and hydrogen re-equilibration with minerals. There would be a good chance that some hydrous minerals might form in the sample container and so on. Such conditions as (c) might well be tolerable if the water was from Mars but the addition of terrestrial water is again very bad. I would consider this alternative not as good as alternative (b) but better than alternative (a), heating in an interplanetary vacuum. I should like to stress that temperature accelerates processes usually in an exponential way whereas time is much more gentle on rates. The lower the temperature of sterilization, the better I would like it.

Generally speaking then samples from Mars would be extremely valuable almost irrespective of what is done to them in terms of temperature. On the other hand as a general principle the less is added and taken away from them on their way to Earth the better. It appears to me that this is mainly a choice as to which one prefers, high temperature and short sterilization time or relatively low temperature and long sterilization time. I definitely prefer the latter.

As to what research is needed to provide knowledge of the conditions of the preservation of the samples with the type of sterilization, it seems to me rather obvious that one can simply mix all the various things that are listed in the report and subject them to these different sterilization processes.

It is almost impossible for me to sit down and consider all the various molecules that I think exist on Mars and evaluate them from the point of view of what sterilization processes will affect which ones more readily. I clearly believe that stable isotope data of hydrogen, oxygen, carbon, nitrogen, silicon, calcium, etc. will be extremely useful in helping understand the various processes that go on on Mars and the temperature under which they are going on. The preservation of the integrity of these isotopic abundances in the various phases would be most critical. I think that it would probably be best preserved if the Mars sample is sealed and heated to 150°C. Another possibility would be to bring the samples back to Earth and subject them to other forms of sterilization

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like soft X-ray radiation which might kill all biological life but still preserve the integrity of the chemical and isotopic compositions. Such a possibility is not mentioned in your letter and it seems to be that such should be considered in some cases.

I would probably be able to discuss this a little more intelligently in a face-to-face discussion. I would therefore be happy to get together with you perhaps at the lunar conference regarding this matter. In any case feel free to phone me.

Good luck on your Mars project. Best regards.

Yours truly,

Sam

Samuel Epstein
Professor of Geochemistry

SE:bac

TYPED COPY OF HANDWRITTEN LETTER

JPL Memorandum

TO: Larry Nyquist

FROM: Fraser Fanale

"Low temperature" mineralogy crucial/clay and iron hydroxide etc., as coatings on surfaces. These are easy to make in Martian environment and tell us more about surface condition than details of high T petrology.

This stuff is delicate, and would be destroyed at intermediate temperatures 300°-500°C. ∴ low T long time advisable.

We don't want to lose the gas coming off and we want to give the rock a chance to reconstitute itself; e.g., replacement of interlayer H_2O in montmorillonite. On other hand, we fear that an unaltered igneous rock might "stew in its own juice" and get altered during sterilization. Therefore, cold trapping of volatiles is best.

Obviously we need to put various mineralogies through these hoops. One neat way to do this would be to run various candidate assemblies through the various sterilization time/temperature cycles <u>twice</u> on a Differential Scanning Calorimeter/Evolved Gas Analyzer. Then one could tell the effect (from the endotherms and simultaneous EGA peaks) that the time/temperature cycles and volatile trapping mechanisms each have on various assemblages in terms of producing <u>irreversible</u> changes. I have such a setup and will let you know if I get around to getting any good data on this.

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
Geologic Division
Branch of Experimental Geochemistry and Mineralogy
345 Middlefield Road, Menlo Park, California 94025

March 13, 1974

Mr. William C. Phinney
ATTN of: TN7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

I have just turned my attention to your memo of February 19 concerning possible effects of sterilizing a returned Martian sample prior to arrival on Earth. Owing to the lateness of this reply and pressure to prepare several other reports this week, I will have to make my comments short.

I assume that other consultants have enumerated the many reasons for wanting to determine the petrography, mineralogy, oxydation state, and degree of hydration of the various materials in the sample at the time of collection. My main area of expertise lies in the field of hydrothermal water-rock reactions, and I shall comment only on option C, "Heat sterilization in a sealed container with water added to produce 80% relative humidity above the sample." My opinions are based mainly on several experiments (unpublished data) in which I have reacted individual minerals and rocks with water and salt solutions for various lengths of time at temperatures ranging from 200° to 300°C and 100% humidity. Under those conditions, the amount of reaction depends in great part upon:

1. The temperature and duration of the experiment - a very rough empirical rule is that reactions double their speed with an increase in temperature of 10°C (at 300°K) (S. W. Benson, 1960, p. 66, The foundations of chemical kinetics, McGraw-Hill, N.Y. 703 p.)

2. The energy driving give reactions to occur - Phases that are not far from equilibrium or that require high activation energies will undergo little, if any reaction. On the other hand, highly metastable materials such as glasses tend to react very quickly. Glass hydrates, devitrifies, and reacts with adjacent crystalline phases to form new minerals, generally zeolites and clays.

In regard to the Martian sample, I think that there generally would be more reaction at 300-350°C in one day than at 200-250°C for one week. Similarly, there would be more reaction at 200-250°C for one week than at 150°C for one month. However, in all cases, there could be drastic changes in the oxidation state of iron. All of the original iron oxide minerals might be destroyed and new ones formed. Any glass in the sample (volcanic and meteor impact melt) would certainly hydrate and probably would devitrify (especially at 200°C+). There is a good chance that the glassy material would react with crystalline silicate rock fragments as well as carbonates and sulfates. Alteration products are likely to be many different zeolites. Any original sublimates are not likely to survive. Montmorillonite may react with carbonates and sulfates to yield new calcium and magnesium silicates. This would be particularly true above 250°C.

I hope that these brief and sketchy comments will be of some help to you.

Sincerely,

R. O. Fournier

Robert O. Fournier

HARVARD UNIVERSITY
DEPARTMENT OF GEOLOGICAL SCIENCES

CLIFFORD FRONDEL
Professor of Mineralogy
Curator, Mineralogical Museum

GEOLOGICAL MUSEUM, 24 OXFORD STREET
CAMBRIDGE, MASSACHUSETTS 02138

March 8,1974

Dr. Robin Brett, TN7
Manned Spacecraft Center,
Houston, Texas,77058

Dear Robin :

With respect to the Martian sample,I will confine my remarks to the sampling,adsorptive nature and sterilization of particulate material in the sub-micron and colloidal range of size.

The Martian surface environment must act as an efficient colloid mill. The high wind velocities, low atmospheric pressure and very low temperature should reduce the surface particulate material in part to sizes far below those attainable by natural processes on Earth or on the Moon. The low temperature produces embrittlement and restrains chemical attack. On Earth, very fine material is ultimately removed by chemical attack,although it may have a relatively long life span in very dry and/or very cold environments. On the Moon, where very fine material could be produced attending impacts, the high temperatures tend to destroy it by coalescence or vaporization.

The Martian fines are of interest because of the possible content of microscopic spores of biological origin. They are of great interest both mineralogically and,in particular,in their content of surface adsorbed material.

Particulate material in the sub-micron range, especially below about 1000A,because of the large surface area relative to the volume of the particles,stores a relatively large amount of adsorbed material. What would be adsorbed depends on what was in the Martian atmosphere and on the chemical and physical nature of the adsorbent.

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Since adsorption can be highly selective, some things present in the atmosphere - possibly organic molecules - could be wholly removed and stored in this way.

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(1). With regard to properties that should be measured on a returned Martian sample of sub-micron material

(a) Particle size and shape examined by SEM and TEM techniques.
(b) Identification of the specific mineral phases by electron diffraction, etc.
(c) Examination for spores or other biological materials
(d) Evaluation of biological hazards
(e) Bulk chemical analyses of the sample and of individualized fractions thereof.
(f) Study of amount and kind of adsorbed material

(2) Thermal sterilization involves the following matters :

(a) Desorption of material held on surfaces. The temperature needed for desorption depends on the nature of the adsorbent and adsorbate or, more generally, on the nature of the forces holding the material to the surface. Molecular compounds held by van der Waals forces would come off at temperatures probably well below 200°C; chemosorbed material may be retained at temperatures well over 200°C. Changes in the adsorbent itself brought about by thermal treatment are a factor here.

Thermal sterilization of the fines should be done stepwise, say at 25°C intervals upwards from room temperature, with removal of the desorbed material from the container at each step.

Sampling of the adsorbed gases, etc., may perhaps be best done on the Martian surface. A relatively large sample could be heated in a sealed container brought for the purpose - the heat provided by a built in chemical source - with the desorbed material trapped out cryogenically in a receptacle that can be sealed, detached and returned. The Martian environment certainly is cold enough to trap out at least the heavier molecules.

(b) The particulate material presumably would be enriched in mineral components resulting from the chemical breakdown, on the Martian surface, of primary igneous minerals. They hence could be expected to contain H_2O, OH and CO_2 as essential primary constituents. Compounds containing such constituents in general are not very stable thermally. An upper limit for thermal sterilization precluding such decomposition is not easily stated, especially if the particle size is extremely small, and if the nature of the substances is not known beforehand. The lower the temperature of sterilization the better, with a maximum of 150°C probably OK, over 250°C probably bad, and over 350°C certainly bad. Because of the relatively large surface area, sintering effects also come into question at the higher temperatures. The thermal decomposition of any organic compounds present is an added problem.

(3). Studies of the following matters preparatory to a Mars mission would be helpful :

(a) The sampling of finely divided air borne particulate material is a well developed field in which NASA doubtless could get good advice from the AEC.

(b) The sampling of surface deposits of very finely divided particulate material, especially if incoherent, with preservation of internal layering, is not a well developed field. Impregnation by a liquid polymerizing at low temperatures might preserve some information.

(c) Laboratory studies should be made of the adsorption and desorption of O, N, A, He, CO, CO_2, NH_3, CH_4 and CH_2O on powders of known particle size, using goethite, hematite, siderite, quartz, pyrolusite, kaolinite, diaspore, montmorillonite, plagioclase and pyroxene.

(d) Laboratory studies of the thermal decomposition of goethite, etc., as a function of particle size, both in vacuum and at 1 atm. CO_2 or air.

Finally, if the LRL is to be reconstituted with the original staff and equipment, and the Martian sample examined therein, research should be done on where to move Earth's population so that it has some chance of survival.

Best regards,

Clifford Frondel

FACULTY OF ARTS AND SCIENCES
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15260

DEPARTMENT OF EARTH AND PLANETARY SCIENCES
506 Langley Hall

March 14, 1974

Dr. Robin Brett
NASA - Lyndon B. Johnson Space Center
Houston, Texas 77058 ATTN: TN7

Dear Robin:

I enclose the notes on the possible effects of various proposed sterilization procedures on the magnetic information carried by Martian samples. It is my understanding in doing this that others will consider the question of whether Martian samples should be returned to earth as opposed to being studied in some latter day sky lab, etc. Sorry these notes are, as usual, late. They slipped by in my schedule somewhere.

As a starting point, we may ask what we may learn from Martian samples by magnetic observations. By now it is clear from terrestrial, lunar, and meteoritic samples that if we can understand their primary NRM, or even secondary NRM associated with a particular event in the sample's history, we can obtain a record of ancient magnetic fields experienced by the rock. Hence, the principle aim in the Martian work would presumably be to get a record of the ancient Martian magnetic field. If we ever get bedrock samples, they may give results relevant to structural geology of one sort or another. In addition, we can use magnetic observations such as hysteresis classification which characterize the magnetic phases to help our understanding of the rocks themselves.

Assuming that our aim is to obtain a record of the ancient field of Mars and to characterize the magnetic phases of the rocks, we now need to consider the necessary observations. These are, quite simply, the measurement of the NRM and its demagnetization characteristics, and of such basic rock magnetism parameters as saturation magnetization, saturation remanence, susceptibility, etc., which permit characterization of the magnetic phases.

At this point we need to make use of the current wisdom for the Martian surface to give us some idea of the nature of the probable carriers, and the environment in which they were formed. An important parameter for the magnetic observations is the diurnal temperature cycle. Unlike the lunar diurnal cycle, its maximum is not significantly greater than the temperature in the laboratories in which the rocks will be measured. This means that any heating will degrade the magnetic results. The Martian samples are unlike lunar samples which have been thermally cycled to 100°C in the present low surface fields of the moon, so that they have essentially been thermally demagnetized to approximately 100°C. Hence, subsequent heating of lunar samples to 100°C should not destroy useful information due to simple thermal demagnetization. In contrast, we will destroy potentially useful information by heating Martian samples since we will certainly thermally demagnetize them. Nevertheless, heating Martian samples to 150°C or even to 300°C may

still not be a disastrous treatment providing that the magnetic carriers are not seriously degraded by the heating. If the heating were carried out in a shielded region, then this could effectively be a first step in a thermal demagnetization, a procedure which would probably be carried out eventually anyway. Even if it were carried out in a magnetic field, this magnetization could possibly be unscrambled eventually.

The most difficult problem then is to assess the effect of heating on the magnetic phases themselves. If, as the current wisdom suggests, the NRM may be carried by hydroxides and hydrated salts, then heating even to 150°C, could be disastrous. The properties of the relevant mineral species are relatively well known; their Curie points and fields of stability are, in part, in this low temperature range (20-300°C). There does not seem to be much point in giving detailed consideration to particular minerals, in view of our very limited knowledge of Martian surface. Suffice it to say, that if these compounds are really important, then heating to even 150°C may be disastrous. If, on the other hand, current wisdom turns out to be unwisdom and most of the NRM is carried by iron and iron-nickel, or even Fe_3O_4 or Fe_2O_3 hematite, heating to 300°C will be a relatively unimportant problem and good magnetic data should be obtainable.

In summary:

	ASSUMPTIONS	
Heating	1) Magnetism carried by compounds of low temperature stability	2) Magnetism carried by Fe°, FeNi, Fe_3O_4 and Fe_2O_3
150°C	Bad	OK
200-250°C	Worse	OK
300-350°C	Probably disastrous	OK providing care is taken to avoid oxidation of these phases
Incandescent	Forget it!	Forget it!

dehydration

I hope these comments will be of some use to you. Perhaps we should get together with Dave or a few of the other members of the magnetism club and talk about this at the Conference next week.

All very best wishes,

Michael Fuller
Professor

lkt

cc: Dr. King

University of Hawaii at Manoa

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March 1, 1974

Dr. Robin Brett
Lyndon B. Johnson Space Center
NASA
Houston, Texas 77058

Dear Robin:

About the Martian samples: I should think drying part of them at 150°C, with splits heated with water vapor present, would be quite reasonable in terms of preserving most stuff. I don't think it would do much to montmorillonites, except take out the interlayer water. Too bad interlayer water can't be measured; at 25°C the last two water layers are lost at less than the saturation pressure for water -- in fact water content is a rather delicate measure of vapor pressure. Anyway, I assume direct measurements will be made of H_2O pressure in situ. And the montmorillonites will take it back up again.

Abundant iron oxide, as well as traces of O_2, would seem to preclude much $FeCO_3$. The CO_2 pressure is OK, but $FeCO_3$ oxidizes with mere traces of oxygen at a pretty good clip. Color change of the samples with 150°C drying from brown to red would be good indication of goethite originally. By the way, it is still not clear whether FeOOH or Fe_2O_3 is the stable species at 25°C in presence of water. But on Mars, with low H_2O pressure, hematite would be expected.

It would be an interesting exercise, for which there is not time now, to calculate expected weathering phases at H_2O vapor pressures less than that for liquid H_2O at low temperature. I suspect people like Danny Milton already have played that game.

These are about all the comments I have at the moment. I could probably respond better to direct questions than make suggestions.

Cynthia and I send our best.

Sincerely,

Robert M. Garrels

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7 March 1974

Dr. Everett K. Gibson, Jr.
Code TN7
NASA L. B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

I am sorry to be so late in responding to your letter of 15th February, but with the end of the term upon me I have been seriously swamped with chores related to the two courses I am teaching. Consequently I have not had a chance to organize my thoughts on the sterilization problem very completely, nor have I put together supporting data of the kind you would like to have. Nevertheless, under the assumption that something is better than nothing, I would like here to respond to the very interesting questions you raise.

As background information, let me point out that our primary interest in a returned Martian sample would lie in the general area of petrogenesis and studies of clastic transport and mixing processes, as it does for the lunar specimens. We would like to know the compositions of the various types of soil particles and rock fragments present in the returned sample, reading "compositions" as meaning not only chemical but also mineralogical compositions, including such features as structural states of minerals and the degree and nature of abraison of grains. Others may well have other interests and inherent requirements, but I shall treat our requirements based on our interests. I think it is obvious that these properties are of extraordinary, perhaps primary, importance in drawing inferences about the planetary evolution of Mars.

Sterilization by heating to incandescence, even for a very short time, would be grossly destructive of a great deal of important information of this kind. I simply cannot envision that anyone could do control experiments adequate to tell us how such treatment would change the contents of elements like the alkalies, halogens, carbon compounds, water, etc., and those components are likely to be very informative in outlining a history of the Martian soil (see, for example, the arguments in the accompanying reprint; the history of water contents in the Martian shallow lithosphere are probably written in part at least in the hydrated minerals of the soil). Furthermore, heating to incandescence would certainly destroy the records originally held by the mineral phases in the soil, records of the kinds of rocks available for incorporation in the regolith and of the transport processes which moved them about. Clay minerals, which should be an important and very interesting component of the Martian soil, would be destroyed by such a treatment. I think it is simply unacceptable as an alternative.

Sterilization in a sealed container with 80% relative humidity would probably not change significantly the overall composition of the sample, but would grossly perturb both the mineralogical character and the distribution of elements among grains. It

would probably destroy micro-scale surface features which would if preserved help greatly to understand modes of transport of clastic materials. It goes without saying that such treatment would destroy any records of the history of f_{H_2O} in the Martian atmosphere that might be present in the sample, and it is easy to see that such records are at least of as much interest to exobiologists as to the rest of us. I conclude that while slightly less destructive than heating to incandescence, this approach is also unacceptable.

Heating in vacuum for any substantial period is likely to dehydrate clay minerals (but probably not goethite -- see the arguments about kinetics in the enclosed reprint), but judging from the substantial amount of information which can be obtained from dehydrated or partly dehydrated clays in carbonaceous chondrites, that is not a major objection. I judge that, especially at 150 to 250 °C, there will be no significant destruction of information on chemical composition, and it is easy to predict that there will be no damage worth mentioning to microscale surface features. Consequently, I vote for one form or another of these treatments. Obviously we need to undertake control experiments to establish that a protocol of that kind will reliably sterilize the sample, and in so doing we could usefully test its effect on the properties I have mentioned. If I can be of assistance in carrying out such control experiments, such as by running INAA analyses before and after, please let me know. We would probably need minor funding to do very much of that kind of work, but could sneak a few comparison samples in under our lunar funding.

Best regards,

Gordon

Gordon Goles

JOURNAL OF GEOPHYSICAL RESEARCH VOL. 75, NO. 35, DECEMBER 10, 1970

A Re-examination of the Stability of Goethite on Mars

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New estimates of the equilibrium vapor pressure curve and of the kinetic parameters for the goethite-hematite system are given. Goethite is apparently unstable at the surface of Mars during the daytime, but is stable deeper in the soil where the temperature is constant. Because of stirring by winds, these two zones presumably are coupled together. For almost all plausible kinetic models, little goethite will be permanently dehydrated during the lifetime of Mars, either because the rate of rehydration in the subsurface layer is comparable to or greater than that of dehydration at the surface or because of the slowness of the latter process. Goethite may exist at the surface even though it is unstable, for the dehydration time is much greater than the likely characteristic time for vertical mixing by winds. To within order-of-magnitude precision the dehydration-rehydration cycle appears to be balanced and if so buffers the time-average content of atmospheric water vapor.

The mineral goethite (or limonite, a rock composed chiefly of goethite) closely matches the photometric and polarimetric properties of the Martian surface [*Dollfus*, 1957; *Sagan et al.*, 1965; *Binder and Cruikshank*, 1964; *Pollack and Sagan*, 1969]. *Adamcik* [1963] estimated conditions for stability of goethite against dehydration into hematite and suggested that the content of atmospheric water vapor on Mars is buffered by this reaction. However, more recent studies by *Fish* [1966], *O'Connor* [1968], and *Berner* [1969] have indicated that goethite would be unstable under the conditions on Mars. Thus on very fundamental grounds they rule out the presence of goethite.

In this paper we reconsider the stability of goethite on Mars. Previous investigators have considered only the conditions at the very surface of Mars, whereas we treat also conditions in the subsurface soil layers. In addition, they have not investigated kinetics of the approach toward equilibrium. We begin by establishing limits on the equilibrium vapor pressure curve of goethite as well as presenting values for the rate parameters of the dehydration and rehydration reactions. Applying these results to Mars, we investigate stability relations at and below the surface, estimate the degree to which dehydration at the surface is balanced by hydration below, investigate the kinetics of the reactions, and finally reconsider Adamcik's suggestion that the goethite-hematite system buffers the atmospheric water-vapor content on Mars.

THERMODYNAMICS CALCULATIONS

The reaction that determines the partial pressure of water vapor when goethite is in equilibrium with its anhydrous derivative, hematite, is

$$2\mathrm{FeO(OH)} \leftrightarrows \mathrm{Fe_2O_3} + \mathrm{H_2O\ (vapor)} \qquad (1)$$

For calculation of the equilibrium curve one requires: (1) the molar volumes of each of the phases, (2) either an experimental determination of an equilibrium point ($\Delta G = 0$) or a measurement of the heat of reaction (ΔH), and (3) the molar entropies and heat capacities of each of the phases. The symbol G refers to the Gibbs func-

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tion, and Δ denotes the difference in the value of a given quantity between the two sides of equation (1). As the molar volume of water vapor V_{H_2O} is large compared with the molar volume of the solids, we simply set ΔV equal to V_{H_2O}. At high pressure, allowance must be made for the departure from ideal gas behavior.

A point on the equilibrium curve was inferred from measurements of an equilibrium point for the goethite–hematite–*liquid*-water system. For pressures ranging from a few to a few thousand atmospheres, *Posnjak and Merwin* [1922] and *Smith and Kidd* [1949] obtained a temperature value of 125°C at the equilibrium position. The equilibrium temperature had no apparent pressure dependence. Furthermore, Smith and Kidd were able to reverse the reaction, i.e., to approach equilibrium from both directions, so that the reliability of their determination seems well established. The above results imply that ΔG equals zero for the iron oxide–liquid-water system at a temperature of 125°C and a pressure equal to the saturation pressure of water at this temperature. As ΔG is also zero at this same temperature and pressure for a liquid-water–gaseous-water system, ΔG for equation 1 is zero under these conditions.

To estimate ΔS for the goethite-hematite system, we assumed that it equaled a well-determined value of ΔS for the dehydration reaction of phases isostructural with hematite and goethite. This seems a reasonable approximation since the configurational entropy changes, which dominate ΔS, are similar in the two cases. Disapore, AlO(OH), is isostructural with goethite and dehydrates to corundum, which is isostructural with hematite. The entropies and heat capacities of diaspore and corundum are found in *Kelley* [1960], and the ΔS of dehydration can be calculated easily. We assume that contributions of spin entropy to the total entropy of the solid phases are similar for goethite and hematite. J. T. O'Connor (private communication) has pointed out that spin contributions to the total entropies might be as large as 25% for these phases. Magnetic susceptibilities differ between hematite and goethite by about 30%, so that perhaps our estimate of ΔS is in error by 7% or so. Such an error would not affect our conclusions in an important way (see below).

The thermodynamic equations needed to calculate the equilibrium vapor pressure curve are as follows:

$$\Delta G(T^*, P_0) = \int_{p^*}^{P_0} \Delta V \, dP = RT \ln (f_0/f^*) \tag{2}$$

$$\Delta G(T, P_0) = G(T^*, P_0) - \int_{T^*}^{T} \Delta S \, dT \tag{3}$$

$$P_e(T) = \exp (-\Delta G(T, P_0)/RT) \tag{4}$$

where T, R, P, and f are temperature, the gas constant, partial pressure of water vapor, and fugacity, respectively. The superscript * and the subscripts e and 0 refer to values at the known equilibrium point ($\Delta G = 0$), the equilibrium value at any temperature, and conditions of *STP*, respectively. For small changes in temperature (less than 100°K), ΔS is essentially constant. For large changes, ΔS can be expressed as a linear function of T. At low pressures, water vapor behaves ideally, allowing us to use pressure rather than fugacity.

The curve constructed from the data and assumptions described above is shown in Figure 1. Superimposed on the equilibrium curve of goethite/hematite is the vaporization curve of pure, liquid water. For temperatures above 125°C the vapor-pressure curve for goethite lies above the saturation curve. Accordingly, condensation will always prevent the realization of the high vapor pressure needed to stabilize goethite above 125°C. Thus, in the laboratory we cannot directly measure the equilibrium vapor pressure curve at temperatures in excess of 125°C. Moreover, on the basis of the rate parameters given below, the time to reach equilibrium below this temperature is quite long. For these reasons it would appear to be most difficult to measure directly the equilibrium vapor pressure of the goethite-hematite system; consequently it is better to use more readily observable thermodynamic properties to deduce the phase curve.

Figure 1 also indicates that for terrestrial goethite deposits the mineral will remain stable against dehydration as long as the humidity is not too low. The value of ΔG at 1 atm partial pressure and 298°K is +3413 cal/mole.

The assessment of goethite's stability on the earth is greatly complicated by its interaction with liquid water, whose pH may be other than neutral and which might contain a significant quantity of impurities. *Schellmann* [1959] and *Atkinson et al.* [1968] report that formation of

goethite is favored in basic solutions and hematite is favored in acidic ones. Goethite, however, is known to form in mine waters with pH as low as 3, although its formation may be a kinetic rather than an equilibrium phenomenon. Impurities may also favor the precipitation of an FeO(OH) polymorph at low pH's (Atkinson et al.), but we could find no case in which impurities favor the precipitation of hematite at high pH's.

Some estimate of the error introduced by the above approximation for ΔS may be obtained by comparing the values for ΔS of two pairs of isostructural substances for which the entropies are known. Brucite, $Mg(OH)_2$, crystallizes with a CdI_2 structure, as does portlandite, $Ca(OH)_2$, whereas their anhydrous derivatives, periclase, MgO, and lime, CaO, crystallize with NaCl structure. At a temperature of 298°K and one atmosphere partial pressure of water vapor, ΔS for the dehydration of $Mg(OH)_2$ to MgO equals 36.57 entropy units, and the corresponding value for the calcium pair is 34.68. Thus there is only 5.5% difference in their values of ΔS. If such an error is present in our estimate for the goethite-hematite transformation, the equilibrium pressures at 300°K and 220°K would have values of $3.2 \pm 1.1 \times 10^{-3}$ atm and $3.6^{+3.3}_{-2.4} \times 10^{-7}$ atm, respectively.

Critique of Previous Thermodynamic Calculations

We now comment on some previous attempts to determine the equilibrium vapor pressure curve. *Schmalz* [1959] employed the same set of thermodynamic parameters as we did. Apparently, he approximated the pressure at the equilibrium point in Posjnak and Merwin's experiment as 1 bar instead of its actual value of somewhat more than 2 bars. To obtain the slope of the phase boundary for the goethite–hematite–liquid-water system and hence ΔS, he compared Posjnak and Merwin's equilibrium temperature at moderate pressures with his results at pressures over 2 orders of magnitude larger. This is a somewhat dubious procedure, since the phase boundary may have significant curvature over such a large range of pressures.

In his derivation of the equilibrium vapor pressure *Adamcik* [1963] estimated ΔS by analogy to typical hydrated minerals. We feel our approach is superior in this regard, since goethite and hematite are harder and denser than many other hydrated minerals. Generally, entropy values reflect these physical characteristics. The aluminum compounds used by us to estimate ΔS have hardness and densities similar to those of goethite and hematite. In addition Adamcik used *Sabatier*'s [1954] value of enthalpy for the dehydration reaction. As shown in Table 1, other investigators have obtained significantly different values for this variable, and hence it seems to be a rather poorly known quantity at present.

Fish [1966] used various combinations of thermodynamic variables to set limits on the phase curve. These include Sabatier's enthalpy

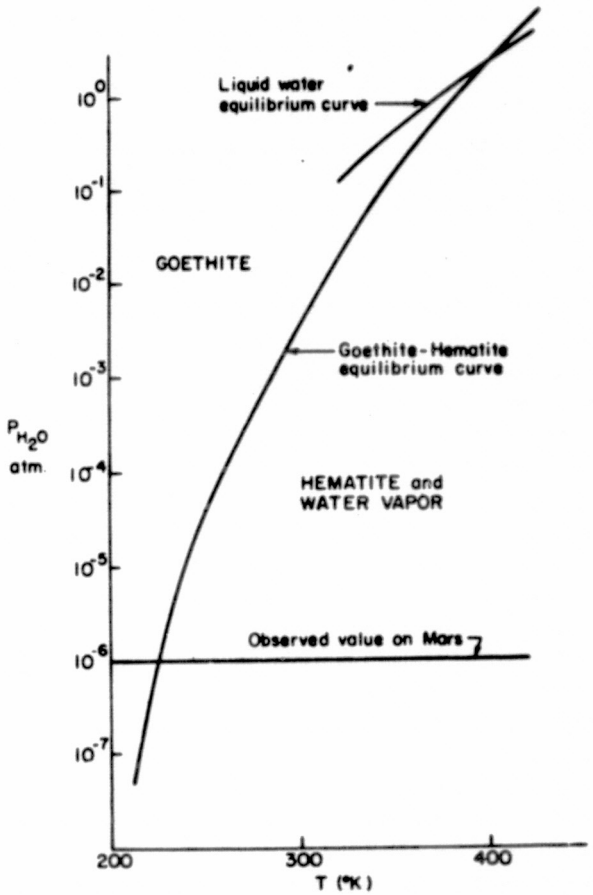


Fig. 1. Equilibrium vapor pressure curve for the goethite-hematite system. At a given temperature when the actual partial pressure of water vapor lies below the equilibrium curve, hematite is stable and goethite decomposes to hematite and water vapor. The converse is true when the partial pressure exceeds the equilibrium curve. Also indicated in the figure are the saturation curve for liquid water and the 'observed' partial pressure of water vapor at the Martian surface.

TABLE 1. Measurements of the Enthalpy Change of Dehydration for Goethite

Investigator	ΔH(298°K), cal/mole
Barshad [1952]	+18,100
Ferrier [1965]	+12,686
Sabatier [1954]	+15,490

estimate and Schmalz's determination of ΔS and thus are subject to the criticisms given above.

O'Connor [1968] based his calculation on unpublished determinations of the specific heat of goethite at temperatures ranging from near 0°K to room temperature. A possible difficulty with this method is a significant contribution to the specific heat from the heat of sorption of physically bound water [*Pollack et al.*, 1970; henceforth paper 1]. This type of water, not to be confused with the chemically bound component, may have been present in large amounts, since the sample studied was a powder. In any event, O'Conner's results seem hard to understand. A simple extrapolation of his published data points leads to pressures at 125°C far in excess of the value implied by Posjnak and Merwin's and Smith and Kidd's studies of the equilibrium point of the goethite–hematite–liquid-water system.

Berner [1969] questions the results obtained by Smith and Kidd. His findings, based on the solubility of goethite and hematite in moderately strong HCl solutions at 85°C, indicate that hematite is the stable phase under nearly all geological conditions. Smith and Kidd record a reversed point, but Berner suggests that the gels used as starting materials by Smith and Kidd may have been identified incorrectly.

We disagree with Berner because of the following points:

1. The compositions of some of the gels used by Smith and Kidd as starting materials, as well as products of the experiments, were checked by means of X-ray diffraction.

2. The reaction was reversed a second time by placing hematite in pure water and allowing two years for the hydration to occur. The results were again checked by means of X-ray diffraction.

3. The free energy of solution of a compound is related to the *solubility product* of that compound. The *solubilities* of compounds may be compared directly only when their stoichiometric formulas are identical. Such is the case of aragonite and calcite or of quartz and cristobalite. Goethite is isostructural with diaspore [*Lima de Faria*, 1963], and neutron-diffraction studies of diaspore have shown that the correct formula for diaspore is AlO(OH) [*Busing and Levy*, 1959]. We may therefore assume that goethite is FeO(OH). Clearly, the solubility of goethite is dependent on the activity of hydroxide ions in solution. This is obviously not the case for hematite; consequently Berner's conclusion on the stability of hematite, in which he relies on *solubilities*, is invalid.

The invariant point obtained by Smith and Kidd should be considered valid unless the experiments are duplicated and their results disproved.

Kinetics

For our purposes it is important also to obtain information on the kinetics of the hydration and dehydration reactions. We shall first discuss the dehydration reaction and then show how the rate for the hydration process can be readily expressed in terms of the rate for dehydration and the equilibrium vapor pressure.

We can define a rate parameter k_d' for the dehydration reaction as equal to $dW(t)/dt$, the time rate of change of W, the per cent of goethite remaining at time t. k_d' will in general be a function of temperature, particle size (if a powder is being considered), and W. This rate parameter should *not* be confused with the classical 'specific reaction rate.' Of particular interest for the present set of calculations is the dependence on temperature. In accord with the usual convention, we relate k_d' to temperature through the Arrhenius equation.

$$k_d' = C \exp(-E_a/RT) \qquad (5)$$

where C is a constant, R is the gas constant, T is the absolute temperature, and E_a is the activation energy, which may be a function of temperature. Because dehydration rates are extremely small at temperatures of interest, we are forced to rely on studies of dehydration at elevated temperatures.

In paper 1, three independent estimates of the activation energy were presented on the basis of experimental work reported therein and other

relevant data. For a temperature range of 300 to 350°C they find a value for E_a of 33.5 ± 5 kcal/mole; for 225–390°C, 29 ± 2.5 kcal/mole; and for 200–233°C, 22 ± 4 kcal/mole, with the last result being the most dubious. Since it is clear that E_a is not well determined, we shall carry out our calculations below for activation energies ranging between 15 and 40 kcal/mole and consider values between 25 and 33 kcal/mole as the most probable values.

The measurements reported in paper 1 also supply an estimate of the constant C in equation 5 and hence an absolute time scale. The time τ_d required for a powdered sample to dehydrate to e^{-1} of its original weight at 225°K was inferred to be 67 hours. As the particles composing the sample had dimensions comparable to those found in the Martian bright areas [*Morrison et al.*, 1969; henceforth paper 2] we can directly apply this result to Mars. Noting that τ_d scales inversely with k_d', we see from equation 5 that its value at a temperature T will be approximately (compare equation 1 of paper 1)

$$\tau_d = (67) \exp (E_a/RT_e) \cdot \exp [-E_a/R(498)] \quad \text{hours} \qquad (6)$$

The rate parameter for rehydration k_r', which has an analogous definition to k_d', may be obtained in a straightforward fashion. At equilibrium k_r' will equal k_d'. Assuming that k_r' varies linearly with the partial pressure of water vapor, we find the following general expression for k_r' at temperature T:

$$k_r'(T) = k_d'(T)(P/P_e) \qquad (7)$$

where P_e denotes the equilibrium partial pressure and P the actual value. Finally, the net fractional rate of rehydration simply equals the difference between the rate parameters k_r' and k_d'.

$$r_{net} = [(P - P_e)/P]k_d' \qquad (8)$$

where a positive value for the right hand quantity indicates that hydration takes place and a negative sign implies that a net dehydration is occuring.

Stability of Goethite on Mars

We now apply the above results to investigate the stability of goethite on Mars. We first wish to determine the sign of equation 8 for surface and subsurface layers. For the present we restrict the discussion to bright areas. *Sinton and Strong* [1960] (see also paper 2) have found that equatorial regions on Mars undergo large temperature fluctuations over the day, achieving a peak temperature of about 303°K near the perihelion orbital position. With the activation energies indicated above, the rate parameter declines by a factor of 2 in just 5°K, and the rate parameter at the peak temperature will be many orders of magnitude larger than that during the night. Thus the net rate of the reactions at the surface is determined by temperatures quite close to the peak value. According to estimates by *Sagan and Pollack* [1967], the lowest peak temperature achieved by an area at an optimum orbital position is about 285°K. From Figure 1 we see that the effective equilibrium water vapor pressure P_e for surface locales varies between about 1×10^{-3} and 5×10^{-3} atm.

We now compare these values with the observed partial pressure. On the average there seems to be about 15 μ of water vapor on the day side of the planet [*Schorn et al.*, 1967]. When allowance is made for the cooler surface conditions at night and condensation in the upper atmosphere during the day [*Gierasch and Goody*, 1968], we estimate that there is an average partial pressure of about 10^{-6} atmosphere at the surface. Comparing this number with the above estimates of P_e, we conclude that goethite located anywhere on the Martian surface will undergo dehydration to hematite.

However, the situation is different at subsurface locations, sufficiently deep for the diurnal thermal wave to be completely damped. After analyzing the complete set of thermal observations by *Sinton and Strong* [1960], *Morrison et al.* [1969] estimate that the equatorial subsurface layer has a constant temperature of 220°K with somewhat smaller values pertaining at higher latitudes. From Figure 1 we find that P_e is at most 3.6×10^{-7} atm, and hence rehydration should occur at all such subsurface locations. Thus goethite is dehydrated at and near the surface and hematite undergoes conversion to goethite in the subsurface regions.

The atmosphere, the surface layer, and the top portion of the subsurface are a coupled system. The photometric, polarimetric, and thermal studies of Mars cited above indicate that the uppermost layers consist of powdered material. This dust layer must extend to signifi-

cant depths at least in the bright areas, as the quasi-specular component of the radar cross section for these regions is significantly below the value pertinent for solid material [*Sagan and Pollack*, 1965]. As a result of dust storms, which occasionally involve a large portion of the planet, individual dust grains are moved both horizontally and vertically. Consequently material will be exchanged between the surface layer and the upper part of the subsurface region. Also, water vapor present in the lower portion of the atmosphere should be able to diffuse to all depths of the dust layer.

The above discussion suggests that in evaluating the long-term stability of goethite near the Martian surface, one should compare the rates of mass transformation dm/dt in the two temperature regions of the dust layer. The variable dm/dt for a given zone is simply the product of the volume of the zone V and the net fractional rate of rehydration in that zone r_{net}, which is given by equation 8:

$$dm/dt = r_{net} V \tag{9}$$

In evaluating r_{net} we assign a characteristic temperature to each zone. As explained above, the rate parameter is a very sensitive function of temperature. Almost all the dehydration that occurs in the surface layer will occur within 10°K of the peak temperature of 303°K, and we shall employ a characteristic temperature of 298°K. In estimating V we take account of only that portion of the zone with temperatures between 293°K and 303°K. The temperature of the subsurface layer varies very slowly with latitude, and we use an average value of 215°K for this zone's characteristic temperature (paper 2).

The volume of the subsurface layer equals the product of the surface area A and depth of the dust layer $d_\downarrow$. The low value for the quasi-specular portion of the radar reflectivity at 70 cm [*Dyce*, 1965] implies that $d_\downarrow$ is greater than half the electrical skin depth at this wavelength. A study of the microwave radio spectrum of Mars presented in paper 2 implies that the skin depth is greater than three times the wavelength. Consequently $d_\downarrow$ is greater than 1m. An upper limit of several km can be placed on $d_\downarrow$ from a consideration of likely sources of powdered material on Mars [*Chapman et al.*, 1968]. In summary,

$$1\text{m} \leq d_\downarrow \leq 3\text{ km} \tag{10}$$

The relevant formula for the volume of the surface material is

$$V = A\, d_\uparrow\, f_d f_y \tag{11}$$

where $d_\uparrow$ is the depth, and f_d and f_y are the fraction of a Martian day and year, respectively, for which an average surface element has a temperature between 293°K and 303°K. *Sinton and Strong*'s [1960] observations of the diurnal temperature behavior of equatorial areas imply that f_d is about 1/6, whereas a map of theoretical isotherms presented by *Sagan and Pollack* [1967] implies that f_y is approximately 1/10. As f_d and f_y have been evaluated at the surface itself and so are overestimates of the values below the surface, we choose $d_\uparrow$ to coincide with the depth where the peak surface temperature is damped by 5°K. Paper 2's analysis of Sinton and Strong's temperature results implies that $d_\uparrow$ is about 1.4 mm.

Using the above estimates of parameters we can evaluate the rates of mass transformation in the two temperature zones. For purposes of determining the dominant mode of conversion, we initially consider $d_\downarrow$ to be a free parameter and evaluate it by setting the two rates equal to one another. If this value of $d_\downarrow$, $d_\downarrow{}^*$, is below the range indicated by equation 10, there then exists a net conversion of hematite to geothite. Conversely, if $d_\downarrow{}^*$ exceeds 3 km, hematite is then stable on the average, and any geothite present will be undergoing a net transformation to hematite. Also, any hydration suffered by a hematite particle in the subsurface would be readily compensated for when it returned to the surface layer. Table 2 summarizes the values of $d_\downarrow{}^*$ so estimated for a range of activation energies and the resultant assignment of stability. The symbols +, −, and ? in the stability column of Table 2 indicate that goethite is stable, unstable, and of indeterminant stability, respectively. The latter classification arises when the calculated value of $d_\downarrow{}^*$ lies within the permitted range. We see that for activation energies below 20 kcal/mole, relevant to temperatures between 215°K and 298°K, goethite will definitely be stable, whereas above a value of 33 kcal/mole it will be unstable.

Reaction Rates on Mars

To further explore the stability of goethite on Mars, we now investigate the kinetics of the

TABLE 2. Equilibrium Depth $d_\downarrow{}^*$, Net Stability of Goethite, and Characteristic Time Constants as a Function of Activation Energy E_a

E_a, kcal/mole	$d_\downarrow{}^*$, meters	Net Stability	$\tau(g \rightarrow h)$, years	$\tau(h \rightarrow g)$, years	$\tau'(g \rightarrow h)$, years	$F\tau_{eq}$ (1), years
15	4.5×10^{-2}	+	...	2.5×10^{5}	4.7×10^{3}	...
20	1.2×10^{0}	?	$>1.5 \times 10^{9}$	$>1.9 \times 10^{8}$	1.4×10^{5}	3.7×10^{4}
25	3.1×10^{1}	?	$>7.5 \times 10^{9}$	$>1.5 \times 10^{11}$	4.1×10^{6}	1.1×10^{6}
30	7.8×10^{2}	?	$>2.2 \times 10^{11}$	$>1.6 \times 10^{14}$	1.2×10^{8}	3.3×10^{7}
35	2.0×10^{4}	–	6.3×10^{12}–2.2×10^{16}	...	3.5×10^{9}	...
40	5.3×10^{6}	–	1.9×10^{14}–5.7×10^{17}	...	1.1×10^{11}	...

competing processes. We shall first estimate the characteristic time scale $\tau(g \rightarrow h)$ required to convert 50% of the goethite initially present in the dust layer to hematite. Equation 6 can be used to estimate the characteristic dehydration time τ_d of material within 10°K of the peak temperature. Allowing for the fact that only a fraction $f_d f_v$ of the surface zone lies within these temperatures, a time $\tau_d/f_d f_v$ would be needed for 50% conversion of an equivalent depth $d_\uparrow$ or a time $\tau_d/f_d f_v \cdot d_\downarrow/d_\uparrow$ for the whole dust layer in the absence of rehydration in the subsurface layer. Allowing for rehydration, we find

$$\tau(g \rightarrow h) = \frac{\tau_d}{f_d f_v} \cdot \frac{d_\downarrow}{d_\uparrow} \left[1 - \frac{dm_\downarrow}{dt} \Big/ \frac{dm_\uparrow}{dt} \right]^{-1}$$

$$= \frac{\tau_d}{f_d f_v} \frac{d_\downarrow}{d_\uparrow} \left[1 - \frac{d_\downarrow}{d_\downarrow{}^*} \right]^{-1} \qquad (12)$$

In evaluating $\tau(g \rightarrow h)$ from equations 6 and 12, we allow $d_\downarrow$ to assume the range of values indicated by equation 10. The results are summarized in Table 2. We see that for the larger activation energies, which imply definite instability, the characteristic time scales are orders of magnitude larger than the lifetime of the planet, assumed to be about 5×10^9 years. Thus any goethite present initially would have suffered little depletion. A similar situation is true in general for the cases of indeterminate stability if $d_\downarrow$ is less than $d_\downarrow{}^*$. Only for $d_\downarrow$ quite close to its lower bound and activation energies between 20 and 25 kcal/mole will there be an appreciable depletion of goethite over a time interval of 5 billion years.

An analogous calculation can be performed for the characteristic time scale $\tau(h \rightarrow g)$ for 50% conversion of hematite to goethite. Table 2 exhibits the results. For activation energies within the goethite stability zone, hematite would quite rapidly be converted to goethite. However, for the indeterminate region, only for the lowest values of E_a and upper values of $d_\downarrow$ will there be an appreciable conversion in a time of several billion years. We note that unlike the values of $\tau(g \rightarrow h)$, the estimates of $\tau(h \rightarrow g)$ are strongly dependent on the actual partial pressure of water vapor. For the most probable values of the activation energy, 25–33 kcal/mole, an original supply of goethite would not be completely depleted, and in almost all cases little if any would be converted to hematite. Negligible conversion of hematite to goethite would occur over this range at the present partial pressure of water vapor.

The above calculations show that in general there is no thermodynamic rationale for denying the presence of goethite within the dust layers near the Martian surface. However, these calculations imply that goethite is not stable in the surface layers, where dehydration is occurring. It is these uppermost layers that are observed photometrically and polarimetrically in which the presence of goethite has been claimed. To clarify this seeming paradox we evaluate the time required for 50% conversion to occur for a goethite grain located in the warmer, southern hemisphere. Such a particle will experience peak temperatures between 293°K and 303°K for $\frac{1}{6}$ of a day and about $\frac{1}{4}$ of the orbital period. The corresponding characteristic time $\tau'(g \rightarrow h)$ is then $24\tau_d$. Estimates of τ' are given in Table 2. For all cases these times are probably much larger than the likely time required for winds to cause a removal of the particle from the surface layer. Thus if goethite is present, we can expect to see it at the surface, owing to mixing of grains upward from deeper soil zones.

Goethite as a Regulator of the Atmospheric Water-Vapor Content

We have seen above that for a range of activation energies, including the most probable values, an exact balance between dehydration of goethite near the surface and subsequent rehydration in the subsurface layers could occur for depths of the dust layer within the present limits on $d_{\downarrow}$. Such a possibility leads us to reconsider Adamcik's suggestion that the goethite-hematite system acts as a buffer for partial pressures of water vapor on Mars. In the case of the earth, almost all the water is located in the oceans and polar snow deposits, and these act as regulators of the atmospheric water-vapor abundance. If goethite is present in significant amounts on Mars, then it would contain much more water than is present in the atmosphere and possibly in the polar caps. Thus it might assume the role of principle (long-term) regulator.

We can imagine the approach to the present Martian atmospheric abundance of water vapor as follows. Suppose initially the atmosphere contained much less water vapor than it does at present. In this case dehydration of goethite at the surface would dominate over hydration below, and there would be a net outgassing of water vapor into the atmosphere. As the partial pressure increases, hydration becomes more competitive, and eventually an equilibrium will be established such that the magnitude of dm/dt will be identical in the two zones. A similar situation with hydration initially dominating could occur if initially there were a large amount of water vapor present. It therefore seems quite reasonable that an exact balance would be struck.

To explore this possibility further we shall investigate the kinetics of the approach to equilibrium. First, consider the initial condition of a low water-vapor abundance. If we consider only dehydration, the time τ_{eq} (1) required to establish the present level of water vapor will be given by

$$\tau_{eq}(1) = \left[\frac{2\tau_d}{f_d f_v}\right]\left[\frac{\sigma}{F\rho\, d_{\uparrow}}\right] \qquad (13)$$

where the first factor represents the time for *complete* outgassing of the surface layer, σ is the observed projected density of water vapor (7.5×10^{-4} g/cm^2), F is the fractional abundance of goethite, and ρ is the density of chemically bound water in goethite (10^{-1} g/cm^3). Table 2 summarizes estimates of $[F\tau_{eq}\ (1)]$ for activation energies that are consistent with equilibrium. As long as goethite is present in sufficient amounts, τ_{eq} (1) will be less than the lifetime of the planet.

Under the assumption of large-scale equilibrium, the rates of mass transformation are the same in the two zones. Thus the time τ_{eq} (2) required to establish equilibrium with an initially large amount of water vapor will be similar to τ_{eq} (1). More exactly, τ_{eq} (2) is given by

$$\tau_{eq}\,(2) = \tau_{eq}\,(1)\,\frac{F}{F'}\,\ln\left(\frac{P_i}{P}\right) \qquad (14)$$

where P_i and P are the initial and equilibrium partial pressures, and F' is the fractional abundance of hematite. Again, if hematite is reasonably abundant, equilibrium will be established in a time less than the age of Mars. Equation 14 implies that the exact value of τ_{eq} (2) is relatively insensitive to the initial abundance of water vapor.

The characteristic time scales required to establish equilibrium conditions are quite large compared to a Martian year of about two terrestrial years. As a result, seasonal fluctuations in the water-vapor content do not effect the hydration-dehydration cycle. Only the average content is of interest. Conversely, seasonal temperature variations will not lead to fluctuations in the level of atmospheric water owing to an adjustment of the dynamical equilibrium point.

Next let us consider the amount of conversion required to reach equilibrium. In the case of an initially low water-vapor content, only a very modest conversion would be required. A fraction $(\sigma/\rho)(1/d_{\downarrow}{}^{*}F) \leq 10^{-4}/F$ of the initial amount of goethite would be converted to hematite. A more substantial conversion of hematite to goethite would be needed if the initial partial pressure were very large.

There are several competing processes that could prevent dynamical equilibrium from being reached. If goethite is present on Mars, it seems reasonable that there may be several other common hydrates also present, which could establish an equilibrium balance of their own. In general, the least stable of the hydrates will continue to dehydrate till the water-vapor content is sufficiently high to make rehydration a

competing process. Such a situation automatically stabilizes the other hydrates. An exception to this rule occurs when the required amount of water vapor is so high that condensation prevents this point from being realized. In this case, a hydrate of intermediate stability could determine the water content. If the time scale for escape of water from the atmosphere through photodissociation or other processes is small compared with τ_{eq}, then the equilibrium point will not be reached and the less stable hydrates will continue to dehydrate. Finally, outgassing from the interior or accretion of water via cometary collisions could keep the atmospheric water-vapor content above the equilibrium position. We have little information about the above possibilities and at present can only compare the equilibrium values of $d_{\downarrow}{}^{*}$ with the observed value $d_{\downarrow}$, as was done above.

We have considered so far only the properties of the bright areas of Mars. Inclusion of the dark areas will induce little change. Although the peak surface temperatures of the dark areas are about 6°K higher than that of the bright areas, their subsurface temperatures are similarly about 6°K higher (paper 2).

Summary

Regardless of the value chosen for the activation energy, within a reasonable range, an initial supply of goethite in almost all cases will suffer little depletion over the lifetime of Mars. Furthermore, because the vertical mixing times are probably much less than characteristic dehydration times at the surface, a goethite particle stirred up to the surface will suffer little degradation to hematite during its stay there. Consequently goethite could be observed at the surface of Mars. Finally, for a range of activation energies encompassing the most probable values, dynamical equilibrium may exist with dehydration of goethite at the surface being balanced by rehydration in the subsurface zone. If this is so, chemical equilibrium in the goethite-hematite system determines the present time-average atmospheric abundance of water vapor on Mars.

Acknowledgments. We are indebted to Daniel Weill of the Center for Volcanology, University of Oregon for a careful and constructive reading of the manuscript.

This research was supported in part by NASA grants NGR-09-015-023, NGR-33-010-082, and NGR-38-003-10.

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SOME CRITICISMS ANTICIPATED

Committees of this sort usually fall victim to several criticisms. To expedite matters, we list these familiar criticisms with brief rebuttals.

Criticism 1

The committee never addressed fundamental scientific questions in a meaningful way. Instead, it got tangled up in hardware matters.

Rebuttal

We agree that science should be given top priority. We have attempted to do this both in our discussions and in our report. If our enumeration of key scientific questions is less than revolutionary, it is because breakthroughs in science are difficult to formalize, and to produce on demand.

Criticism 2

The committee was manipulated by representatives of NASA centers and supporting contractors. Committee decisions were predetermined.

Rebuttal

We recommend a mission more elaborate--and expensive--than is recommended by NASA Headquarters or Langley Research Center.

Criticism 3

The committee was naive with respect to cost and hardware development. (Note that this criticism implicitly contradicts criticisms 1 and 2.)

Rebuttal

A majority of committee members have substantial prior experience with flight experiments. We have spent a great deal of time considering potential missions and science instruments. If our conclusions are open to debate, it is chiefly because predictions of mission cost and hardware development are so uncertain.

Criticism 4

The committee failed to recognize financial and programmatic realities. (Note thatthis contradicts criticism 2.)

Rebuttal

To some degree, we plead guilty. We have not recommended that which has been prefit to the anticipated NASA budget. Neither have we emphasized a fall-back position which, then, immediately becomes the conservative primary position. Instead, we have presented what we believe to be a cogent argument for a sequence of post-Viking missions, beginning with Viking '79. Although implementation of our recommendations will require extraordinary effort, the proposed mission is not unreasonable.

Criticism 5

The committee never paid serious attention to its task. (By implication, another group would do better.)

Rebuttal

We note that committee members have, almost without exception, attended all of the five scheduled meetings. In addition, subcommittees have visited institutions where flight instruments are being developed. Advice has been contributed by more than 20 additional scientists, most of whom have attended committee meetings.

Criticism 6

The committee had a limited or biased outlook.

Rebuttal

Committee members were chosen primarily to assure a blend of scientific background, experience, and attitude. Biology, geology, and aeronomy are all represented. (We concede that geophysics is inadequately represented.) We have found it refreshingly easy to generate arguments for and against any option: small missions, repeat missions, rover missions, sample return, etc. That we can agree on the recommendations of this report is no small triumph.

Criticism 7

The committee's report is dull and indecisive.

Rebuttal

Our recommendations are specific. They are not truistic. We have tried to make the report not only substantial, but also entertaining.

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(Received January 19, 1970;
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March 13, 1974

Dr. Laurence E. Nyquist - TN7
National Aeronautics and Space
Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Larry:

I am sorry this is going to be a bit late.

I will answer quickly the aspects particularly regarding sterilizing on Ar dating. My experience with heating of samples has been mainly in stepwise heating in vacuum for $^{40}Ar/^{39}Ar$ dating of basaltic rocks, biotite muscovite and hornblende (unpublished data) and a heating experiment in the atmosphere for the effects of heating on the loss of argon from biotite (Hanson 1971, see enclosed). In the biotite heating experiment it can be seen that biotite from a rock heated for 10 days at 600°C in N_2 atmosphere loses about 30% of its argon. In a vacuum furnace muscovite, biotite and hornblende heated to 700°C for one hour, less than 3% of their argon. Basaltic rocks lose up to 12% of their argon at 700°C for one hour, but generally less than 3%. Amirkhanoff, Kandt and Bartnitsky (1961, Radiogenic Argon in minerals and its migration, Annals of New York Academy of Science, V. 91, p. 235-275) have heated feldspars as well as Micas at low temperatures, 100-400°C.

From my experience, I would suggest that dry heating in nitrogen or vacuum at temperatures of 300°C and less for ten's of hours will give less than 1% loss of radiogenic argon from the above minerals and rocks. I would suspect that it would also have a negligible effect on Rb-Sr systematics as much higher temperatures are necessary to see any movement in Rb-Sr system, see Baadsgaard and Van Breeman, 1970, reference in the enclosed reprint. Enclosed is a table of our unpublished results on $^{40}Ar/^{39}Ar$ samples. I have given the first two temperature steps of one hour heating and the percent of argon lost at each step.

Sincerely yours,

GNH

Gilbert N. Hanson

GNH:hf

P.S. I'd have this retyped but I think you would rather have the information right away GNH

FROM $^{40}Ar/^{39}Ar$ STUDIES

SAMPLE	TEMP. °C	% Ar LOSS AT TEMP. STEP
MC 2531 B Basalt	700°C	1.3
	800°C	6.8
MC 2544 B Basalt	700°C	2.95
	800°C	9.37
MCB 87 Basalt	700°C	3.92
	800°C	5.64
AN 3-9 Basalt	700°C	2.79
	800°C	21.63
MN 9 Basalt	700°C	5.19
	800°C	13.26
ON 22 Basalt	700°C	4.79
	800°C	12.50
~~T-164 Basalt~~	~~600~~ °C	1.45
	700°C	4.77
~~ON-22~~	~~800~~ °C	1.71
	700°C	1.24
MN 38 Basalt	700°C	11.66
	800°C	22.24
LS 14 Basalt	700°C	3.38
	800°C	19.10
RP 1 Rhyolite	700°C	3.43
	800°C	11.94
MN 7 Hornblende	900°C	1.9
	1000°C	43.4
NL 25 Hornblende	700°C	.51
	900°C	.73
NL 25 Hornblende	700°C	.85
	900°C	.78

MS254 Biotite	700°C	2.41
	800°C	14.33
MS252 Biotite	700°C	1.20
	800°C	16.37
M 7003 Biotite	700°C	1.62
	800°C	21.67
M 7001 Biotite	700°C	0.66
	800°C	16.39
ms 240a ~~MS 2400~~ Biotite	700°C	1.90
	800°C	16.54
ms 240a ~~MS 2400~~ Biotite	700°C	2.87
	800°C	35.72
ms ~~MS~~ 250 Biotite	700°C	0.96
	800°C	24.87
M 7058 Biotite	700°C	1.91
	800°C	22.39
M 7061 Muscovite	700°C	2.41
	800°C	4.88
M 7047 Muscovite	700°C	0.93
	800°C	3.04
M 7045a Muscovite	700°C	0.90
	800°C	3.21
M 5222 Hornblende	700°C	1.73
	800°C	2.90
M 5220 Hornblende	700°C	0.50
	800°C	1.87
M 5217 Hornblende	700°C	0.50
	800°C	0.49

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March 7, 1974

Dr. Larry Nyquist
NASA
Johnson Space Center
Houston, Texas 77058

Dear Larry:

In reply to your request for comments on the possible effects of sterilization procedures on returned Martian samples, I can only offer brief comments based on areas of my own research, because of the tight time requirements you set forth.

Obviously Martian samples should be analyzed in much the same way lunar samples have been. Studies of various volatile gases have been very important in lunar studies and can be expected to be at least as important in Martian studies. All of these gases will be potentially adversely affected by any of the thermal sterilization procedures you outlined, with perhaps the least damaging of the procedures being the low temperature-long time dry sterilization. One solution would be to do the sterilization under conditions such that all the evolved gases could be collected (under ultra-clean conditions) for later measurement. This, of course, essentially requires duplication of the sophisticated state-of-the-art extraction equipment used by many investigators. This procedure will still destroy much crucial information, as it will mix gases from different phases so that the gas contents of individual mineral phases are no longer determinable. Overall, it would seem more sensible to develop techniques for evaluation of biological activity in space, before the samples are introduced to earth.

As a specific example, consider the K-Ar dating of returned samples. Many silicate phases will retain argon when heated to several hundred degrees for weeks, but there are also many phases, especially hydrous minerals, which will suffer significant Ar loss under these conditions. I have enclosed several reprints which deal with problems of thermal diffusion of argon. There is a very large body of published work on this subject, and I suspect most potential questions can be answered by reference to work already in the literature. On the other, the diffusion characteristics of the other rare gases, all of which are important (solar wind studies, xenon chronology, etc.) are very poorly known and would require further study before being useful in evalution of sterilization procedures.

As far as non-volatile elements (such as those used for major element chemistry, Rb-Sr dating, U-Pb isotopic studies, etc.), I would guess that 150°C dry for periods of several weeks would not produce serious mobility problems. Thus, a significant amount of research could still be carried out on such sterilized samples, but this work would still not in any way substitute for the gas studies, as far as answering many fundamental questions concerning the chronology of Mars.

I'm sorry I can't give your request a more thorough reply but March 8 isn't very many days away!

Sincerely yours,

Stanley R. Hart

Stanley R. Hart

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March 7, 1974

Dr. Robin Brett/TL7
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

Enclosed is a write up of my initial thoughts on a set physical properties measurements which I think would be valuable on a Martian return sample. Initial thoughts regarding sterilization are also discussed and additional information which would be helpful in choosing between alternatives outlined. I hope this is helpful and look forward to further discussions.

Sincerely yours,

Bob Housley

Robert M. Housley

Enc.

SOME PHYSICAL PROPERTIES STUDIES ON A MARTIAN SAMPLE

The ultimate goals in studies of returned Martian material must be to learn as much as possible about the initial chemistry of Mars, about its subsequent chemical and physical evolution, and about its interactions with the rest of the solar system.

Although the Martian atmosphere is dense enough to prevent appreciable interaction of solar wind or solar flare particles and micrometeorites with the surface we must still anticipate that Martian surface material may be considerable more complex than lunar fines. At least the following primary constituents might be present;

1) Meteoritic debris including microtektites and spherules,
2) Volcanic ash,
3) Comminuted primary igneous rocks, and
4) Comminuted hydrothermally altered rocks exposed by erosion or large impacts.

These constituents may all have been altered by weathering and wind erosion processes in past and present Martian atmospheres and thermal regimes. The extent to which the original nature of particles can be recognized and the depth to which many questions can be answered depends on the severity of these weathering and erosional processes. On the other hand the weathering itself may contain information about past atmospheric compositions and temperatures.

In view of the varied possibilities it seems that any measurement that might give unique information about the physical or chemical state

of the sample must be seriously considered at this time. Several such experiments together with the type of information they might give are mentioned below.

Mössbauer Spectroscopy: Determines the valence state of Fe and the identity and relative abundance of major Fe containing phases. Can have unique value in the study of altered and/or amorphous phases and characterization of submicroscopic phases.

EPR: Can detect organic free radicals with high sensitivity. Can be useful in the study of magnetic phases and can detect magnetic remenance in very small samples.

Optical Spectroscopy: Useful for correlation with telescopic observations.

Magnetic Probing: If returned sample is a core this might provide quick information on stratigraphy.

Auger and ESCA Spectroscopy: Might detect evidence of any recent exposure of the grain surfaces to reactive gases, for example, gases associated with volcanic activity.

Gas Interaction Studies: Can be useful in characterizing clay minerals and might provide insight into the nature of Martian weathering processes.

Brief consideration of the temperature dependence of chemical reaction rates and diffusion rates suggests that heating option (a) 150°C (or less) for one month would always be preferable to a higher temperature treatment. The choice of atmospheric environment however does not seem to be as clear cut. Each option would protect certain possible information or constituents in the sample at the expense of others.

It appears that we really need experimental data which will allow us to reliably estimate weathering reactions and their rates on the probable primary sample constituents under reasonable past and present Martian conditions and in the sterilization chamber with the possible atmospheric environment options. A rough guess suggests that one month in a sealed chamber at 150°C might produce weathering effects similar to about 100,000 years on the Martian surface and hence would not lead to any great loss of information.

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March 12, 1974

Dr. Robin Brett
Chief, Geochemistry Branch
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

Please include the following as an addendum to my letter of 22 February 1974.

The thin Martian atmosphere and weaker (than terrestrial) gravitational field may permit relatively "soft landings" of cosmic dust that could be identified by means of solar wind coatings and solar flare tracks. In stagnant areas protected from dust storms there may be a sedimentary history of cosmic dust fluxes relating to fluxes of comets, etc.

Another aspect of the thin atmosphere is that most cosmic rays can build up "air showers" leading to muons, which in term will interact in Martian rocks before decaying. Muon archeology could be done by means of mass spectrometry of specific reaction products, and possibly also by track studies.

I believe it would be useful to calibrate minerals thought to form on Mars. Both accelerator bombardments and long-term annealing experiments would be worthwhile. Clay minerals have never been subjected to track studies before.

Yours sincerely,

P. Buford Price

PBP:mk

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March 19, 1974

Dr. W.C. Phinney Attn: TN7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

Here are some comments on the treatment of Martian surface samples with respect to sterilization procedures and what properties should be measured in a returned Martian sample.

Because it seems possible that the Martian soil contains clay minerals that were hydrated in the past (or possibly hydrated somewhat even now) I think that the lowest temperature sterilization temperature possible would be the best. This is not, of course, to preserve any water that might be present, for that is out under any conditions of sterilization, but to preserve the structures intact as much as possible and to prevent dehydroxylation. The irreversibility of dehydration of terrestrial hydrated clays appears to be related largely to structural re-arrangements that take place at higher temperatures, rather than the simple removal of the interlayer water. I have enclosed a table showing the rehydration characteristics of montmorillonite and vermiculite after being heated to differing temperatures. These are all short-term (less than 24 hour) heating times, but the results certainly show that if the hydrated clays are heated much above 200°C for even a short time their hydration characteristics are irreversibly altered. I would choose the lowest temperature possible, heating in a sealed container at 80% relative humidity. Under these conditions virtually all terrestrial clays are refractory to any significant chemical reaction even for long times of treatment. For example, montmorillonite is unaltered by heating in a distilled water solution at 5 atm. at 165°C for as long as three months Eberl (1970). A small amount will, of course, go into solution, but the bulk phase remains nicely intact. The 80% RH will also help prevent either dehydroylation of structural (OH) or any interlayer hydroxy-metal complexes that might be present - these are very common in terrestrial hydrated clays (Rich, 1968).

The properties that should be measured include: (1) Mineral identification, of course. What the Martian surface material turns out to be like in terms of particle size will determine the techniques used. If much turns out to be very fine grained, a combined x-ray diffraction/petrographic study would probably be most beneficial. If clays are present, the x-ray diffraction method, supplemented by some infrared and electron microscopic work would be best. (2) Chemical analysis of the bulk sample, plus, if possible, chemical analysis of any mineral separates it is possible to make. (3) If enough

Department of Geology

material is present, K/Ar and, perhaps, Rb/Sr age measurements should be made. By analogy with terrestrial soils, chemical alteration of a parent rock to a soil often alters the age little or none ( ), because daughter and parent are lost at the same rate.

I think that if the sterilization procedure used is the lowest temperature possible and in a sealed container with a reasonable relative humidity it will be possible to say a considerable amount about the past availability of water at the Martian surface on the basis of the clay mineral assemblages present (assuming they are!). It would be good, however, to have some really long-term, low-temperature (100-200°C) heating experiments in a hard vacuum of the common clays (both hydrated and non-hydrated) to see what the effects will be on their structure - particularly the re-hydration characteristics of naturally hydrated clays.

Hope this will do you some good. Best wishes.

Sincerely,

John Hower,
Professor

JH:ab

enclosure

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Effects of heating montmorillonite

Exchangeable cation	Preheating temperature					
	103° C	200° C	330° C	430° C	540° C	640° C
Li	17·8	17·8 I	9·5	9·5	9·5	9·5
Na	17·8	17·8	17·8	17·8 I	9·5	9·5
K	18 I	18 I	18 I	18 I	9·9	9·9
Mg	17·8	17·8	9·5 I	9·5	9·5	9·5
Ca	17·8	17·8	17·8	17·8	9·5	9·5
Sr	17·8	17·8	17·8	17·8	9·5	9·5
Ba	17·8	17·8	17·8	17·8	17·8	9·8
La	17·8	17·8	17·8	17·8	9·5	9·5

Spacings in Å. I denotes an irrational series (sign of interstratification).
Data for montmorillonite from Upton, Wyoming, after Greene-Kelly (1953a).

Greene-Kelly, R. (1953a) Irreversible dehydration in montmorillonite. Clay Min. Bull., 2, 52-56

Locality	Exchangeable cation	Treatment	Unheated	Thermal pretreatment			
				200° C	300° C	330° C	400° C
Almeria	H	w	15·1	11·6	11·6		9·9
		e	16·5				16·4
Tidinit	Li	w	12·6		10·3d		9·6
		e	17·3		17·3		17·1 / 9·3
Almeria	K	w	11·8				11·6
		e	13·2			13·2	
Tidinit	K	w	12·1				12·3
		e	13·6				13·9
Tidinit	Rb	w	12·1				12·6
		e	14·3				13·5
Almeria	Mg	w	14·6	11·6	14·6 / 9·7		9·8
		e	16·9	16·9	17·3		16·9d / 9·1
Tidinit	Mg	w	14·8	11·6		14·6 / 9·9	9·6
		e	16·9	17·3		17·3	9·1
Almeria	Zn	w	14·6	11·7	15·1 / 10·2		9·8
		e	16·5		16·7		16·9
Almeria	Ba	w	13·2			13·1	12·2
		e	16·9				16·9
Tidinit	Ba	w	12·3		12·1		12·3
		e	16·9				16·9
Almeria	Ce^{3+}	e	17·1		17·1		9·1

w = rehydrated over 50 per cent sulphuric acid.
e = treated with ethylene glycol.
d = diffuse.
Spacings in Å.
From González García and González García (1953).

González-García, F. and González-García, S. (1953) Modificaciones en propiedades de silicatos: An. Edaf. Fisiol. veg., 12, 925-992.

NB There is little newer work on this subject.

THE UNIVERSITY OF WISCONSIN

COLLEGE OF AGRICULTURAL AND LIFE SCIENCES
Madison, Wisconsin 53706

Department of Soil Science

March 8, 1974

Dr. Robin Brett
National Aeronautics and Space Administration
Lydon B. Johnson Space Center
Houston, TX 77058

Re: Your letter of Feb. 19, 1974

Dear Dr. Brett:

I enclose a brief outline of possible experimentation on Martian silts and clays that should be useful in tracing former planetary climates.

← Now @ Iowa Soil Sci. Dept

Dr. Phil Helmke has an interest in trace element signatures which he can make with NAA, as he did in the lunar program, working with Dr. Larry Haskin.

Effects of the possible sterilization procedures are stated with reference to these types of study.

Dr. David M. Mickelson, glacialogist of the UW-MSN Geology and Geophysical Department, believes that a study of the particle surface morphology by scanning electron microscopy should be carried out to study abrasion patterns bearing on eolian and fluvial transport history.

We would appreciate your keeping us informed on your sampling proposal.

Cordially yours,

M. L. Jackson

M. L. Jackson
Professor of Soil Science

MLJ/bp

Enclosure

Greetings to Dr. Johnson & Dr. Hoekin
MLJ

Evidence from Silts and Clays of Martian Paleoclimate

M. L. Jackson -- U. Wisconsin-Madison

Eolian effects on Mars were confirmed by Mariner 9 (Masursky et al., 1972) and changes in light and dark streaks were confirmed during the course of a dust storm (Sagan et al., 1972). Wind tunnel experiments simulated the light and dark streaks about craters, permitting differentiation of depositional from erosional features (Greeley et al., 1974).

Research: Expectation that the dusts are in the 1 to 100 μm range suggests that chemical isolation (Syers et al., 1968; Jackson, 1969; Henderson et al., 1972) would be needed for oxygen isotopic ratio determination of quartz silt, if indeed, quartz occurs in Martian silt (mainly basaltic composition is the common concept).

Variation of quartz isotopic ratio occurs in silts between Northern and Southern earth Hemispheres in the Pacific (Clayton et al., 1972) and adjacent continental areas (Jackson et al., 1973; Churchman et al., 1974). Higher values in the fine silt quartz in the Northern Hemisphere is attributed to a higher chert content (heavy oxygen) relative to that of igneous and metamorphic provenance (Jackson et al., 1971). The higher chert content reflects continental paleoclimatic history, i.e. residence time in reef-forming tropical and equatorial climates during continental drift northward. Whether Martian silt contains quartz which originated during past periods when liquid water existed (like earth lagoonal-weathering regimes) should be available from oxygen isotopic ratio of fine-grained monomineralic quartz isolates such as my laboratory has specialized in making (Henderson et al., 1972). Cross-correlation of this with the possible formation of clays such as montmorillonite from mafic rocks (Wildman et al., 1968) should be carried out, including oxygen isotopic ratio determination

(Henderson et al., 1971; Weaver et al., 1971). The fate of rare earth elements and transition elements during weathering should be determined (Haskin et al., 1973; Helmke et al., 1973).

The earth hemispheric variation observed in oxygen isotopic ratios concords with well-recognized paleomagnetically determined drifting of the Northern Hemisphere continents through reef-forming tropical and equatorial regions during 2 to 6 x 10^8 years involved in the sediment ages from which the shales, dusts, and soils were formed. Scarcity of limestones and dolomites in temperate latitudes of Southern earth Hemisphere continents attest to their not having passed through the equatorial region since the Precambrian; some intercalated strata of Precambrian marbles in Rio Grande du Sol suggest the possibility of earlier passages. Australia's Great Barrier Reef illustrates reef-building (later to be raised into a continent?) on entering the tropics from the south in the last 10^8 years or so. Isolates of quartz from Martian silty sediments should be studied and might help determine the plate tectonics involved thereon.

Sterilization: Sterilization of Martian silt at 150°C-350°C (conditions a, b, or c) would not have any effect on the quartz oxygen isotopic ratio (Syers et al., 1968; Sridhar et al., 1974), but ignition would. Fe-montmorillonite would be decomposed above 350-400°C, but not below. More common Al, Mg-montmorillonite would survive to 500-550°C. Extensive lunar work shows that 150°C sterilization would volatilize Hg, As, Na, K, and Pb; however, the more refactory elements would not be affected by the sterilization at 150°C and could be traced through any weathering regime that has occurred.

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Determination of the transport history of Martian mineral grains by identification of grain surface characteristics

R. H. Dott and D. M. Mickelson
Department of Geology and Geophysics
University of Wisconsin-Madison

Since the advent of the scanning electron microscope, several workers (Krinsley and Margolis, 1969; Krinsley and Smalley, 1972) have succeeded in identifying characteristic surface features on sand grains which were deposited in different sedimentary environments. Thus far, glacial, eolian, fluvial, and coastal environments have tentatively been identified on the basis of these surface features. This technique is presently being refined (by Dott and Mickelson as well as others) by the study of sand grains from modern sedimentary environments.

The application of the method is obvious for Martian samples. It has been suggested that running water, wind and perhaps other transport agents are responsible for erosional and depositional features seen on Mariner Photographs (Sagen et al., 1973; NASA Summary). Characteristics of grain surfaces should give indications of the relative importance of these sediment transport processes.

Further research must be done on silt sized particles. Until now nearly all research has been on sand grains. Also, most work so far has been on grains of quartz. Other minerals might be more abundant and therefore more appropriate for the Martian samples.

Sterilization should not affect surface features of grains unless grains are fused. We know of no experimental results on this aspect. Rapid temperature change may cause grains to shatter, destroying surface textures.

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United States Department of the Interior

GEOLOGICAL SURVEY
12201 SUNRISE VALLEY DRIVE
RESTON, VIRGINIA 22092
Mail Stop #432

March 29, 1974

Dr. William Phinney, NASA
L.B.J. Space Center
Houston, Texas 77058

Dear Bill:

This will reach you under the oft-used cliche' "too little, too late," but in view of our move and attendant chaos, it is the first opportunity I have had to consider the problem, even feebly.

The only materials I can comment on are the clays and iron oxides. Basically, after mucking about with the stability data for Fe phases at low temperatures I subscribe to the Berner thesis (Geochimica Acta, 1969, p. 267-273) that the stable iron oxide will be hematite, with any sterilization procedure simply hastening the demise of metastable oxy-hydroxide. Similarly, the background material provided suggests that the montmorillonoid phase will be dominated by some sort of "iddingsite", that is, a mix of Fe oxide + nontronite. Others on your list may have more definitive data, but I would suspect that almost any heating performed on such material in the total absence of H_2O vapor will alter the nature of structural hydration, particularly if discrete Fe oxide interlayers, such as in the "dioctahedral vermiculites" of soils, are present. I would recommend experimentation with such materials to ascertain what atmosphere, if any, can compensate, with respect to structural hydration, for the heats applied. Another item with which I have had some specifically bad experience is amorphous silica coexistent with such a phase. Low temperature heating (60°C) caused irreversible dehydration of the silica, with resulting formation of aggregate impossible to disperse for oriented x-ray examination.

I was surprised as the author of the summary that available evidence indicates low abundance of carbonates. However, some calculations on aqueous CO_2 species and guesses for iron hydroxy-silicate (greenalite) suggests (with enormous temerity) that Fe silicate may be stable relative to siderite in the presence of condensate. The sterilization procedures raise the whole spectre of re-crystallization, but I have no idea of the consequences.

Sorry I don't have more.

Sincerely,

Blair

Blair F. Jones

TYPED COPY OF A HANDWRITTEN NOTE

Dr. Everett K. Gibson
NASA-JSC, TN7
Houston, TX 77058

Dear Ev,

I have given your letter of February 15 some thought. There are two major aspects which you wnat us to address ourselves to (1) what studies need to be undertaken on returned Martian samples and (2) how should samples be treated prior to their returned to Earth?

Studies on Mars Samples

It is obvious that no simple investigator can outline a detailed account of what needs to be carried out. A good model to follow is the studies presently being carried out on Lunar returned samples but also to include some of the studies which were initially carried out after Apollo 11 and 12 missions, when there was a possibility that organic coumpounds or traces of water may have been present. In particular, it appears important to concentrate on minerals which characteristically form at low temperatures out of on agneous environment. On earth, these usually become included in sedimentary rocks.

Such sediments may include chlorides, sulfates and carbonates. Lack carbonates would indicate very low pH of solution. Lack of sulfate may indicate low O_2 fugacity and lack of chloride would suggest a very brief period for water contact and leaching. Unlike the earth, where exchange occurs within the ocean, on Mars which many have contained only ephemeral bodies of water K and Mg may be as important as Na and Ca in forming salts.

In addition to soluble salts, one should find clays which arise from agneous weathering of acid volcanics as well as zeolites which form from the weathering of basalt and volcanic ash. Oxidizing conditions should show goethite rich sediment dominant, reducing conditions or anoxic conditions may show abundant troilite. Intermediate conditions may produce, pyrrhotite, greigite on pyrite. Such low temperature minerals could then be used to determine the partial pressure of oxygen in the Martian environment when the minerals formed.

Isotopic Measurements

A variety of isotopic measurements should be performed. (1) δO^{18} and δD separated from water in contact with sediment should be informative in determining exchange mechanisms between oxygen containing minerals and the water. Extrapolating backing the data, one should be able to find a δO^{18} - δD relationship which on earth is responsive to altitude and latitude. One should also be able to determine primitive δO^{18} and δD and compare these values with terrestrial values. (2) δC^{13} in various froms of carbon may tell us if there has been biological cycles. In meteorites, δC^{13} of organic compounds is $\approx$ -17 0/00, on earth values <-30 are known. If organic matter is found, it very important to identify the nature of the process by δC^{13} measurements. (3) $\delta S31$ is a very good indication for biological processess. Sulfide produced would be enriched in δS^{32}, contrary to what has been found in either lunar rocks or meteorites.

Effects of Sterilization

My belief is that low temperature heating experiments will do very little to alter the composition and characteristics of the minerals. From experiments carried out in my laboratory, we believe organic matter decomposes most speadily under dry heat. Heating to 200°C for one week produces CO_2 and other products equal to heating the sample for one worth at 150. It is probable that 150°C will be the minimum acceptable temperature of sterilization. I believe that prolonged heating (1 month or less) under dry conditions, will cause little isotopic exchange or sample distinction. On the other hand, heating in the presence of added water could cause substancial alteration and isotopic exchange in the mechanisms.

I would therefore suggest, that for maximum presentation of the original conditions of the Martian surface it is better to heat at (a) the lowest temperature possible and (b) under dry conditions. I believe that by heating to only 150°C, the ateration may be minimum on negligible in terms of inorganic substances.

Sincerely yours,

Original signed by Ian Kaplan

Ian Kaplan

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER
MOFFETT FIELD, CALIFORNIA 94035

REPLY TO
ATTN OF LPE:239-9

March 4, 1974

Dr. Everett K. Gibson, Jr.
NASA-Johnson Space Center TN7
Houston, TX 77058

Dear Everett:

Thank you for your letter of February 15, 1974, which finally reached me last week. As you know my major interests are in organic geochemistry and organic cosmochemistry, and the sorts of molecules that I have been concerned with are extractable in some kind of solvent and are usually classed as non-volatile organic compounds, (i.e., amino acids, fatty acids, hydrocarbons, etc.). Although your letter does not specify exactly, I presume that at the present time you are not soliciting comments with regard to the effects of sterilization on these kinds of substances but rather are asking me to focus my attention on the alteration in chemical properties of light, volatile elements. I assume this based on a copy of a memorandum by Larry Haskins, dated February 11, indicating the areas of research for which you and others at JSC will be responsible. If I assumed incorrectly please let me know, and I will provide whatever I can concerning changes in the organic chemistry upon sterilization treatments.

As you well know my knowledge about light, volatile elements is not extensive. I rely on Sherwood Chang for sophisticated detail in this area, and I presume that he will respond, as you requested, with a detailed consideration based on the work that you and he have done together. About all I can do at this time is state some generalizations which I think must be kept in mind throughout this research effort.

(1) Returned martian samples must be examined for the same light, volatile elements that have been sought in lunar samples.
(2) The same or similar techniques must be applied so that the data resulting from returned martian samples can be compared directly with what is known about the moon.

2.

(3) Both the organogenic elements (C,N,H,O,S,P) and inorganic volatile elements should be examined, but I would stress the importance of the organogenic elements and their volatile compounds which might lead to information related to the organic history of Mars.

(4) Two general procedures have been used for volatile organogenic elements -- pyrolysis and hydrolysis. Application of these same procedures should be extended to martian samples.

(5) In studies of terrestrial and lunar samples heating as in dry heat sterilization is usually avoided except when contamination can be removed by the heating process. Therefore, there is little experimental data at present with regard to the effects of heat on the residual elements.

(6) For lunar samples your work suggests that heating (dry) at 150°C for 1 month would not alter greatly the results you obtain at higher temperatures in your pyrolytic gas released experiments. At 200-250°C for one week I would guess that the samples would still retain useful information for you. At higher temperatures undoubtedly severe alteration of the residual material would result. If carbides occur on Mars as they do on the moon, I would guess that they would remain fairly stable at conditions below 250°C for all time conditions listed.

(7) Wet heat sterilization would cause problems at all temperatures. Even at 150°C with water I would guess that significant carbide hydrolysis would take place. If carbides are not a significant constituent of martian samples perhaps wet sterilization at lower temperatures could be used, but I suspect that the inorganic geochemistry and mineralogy would suffer.

(8) Experiment must be designed to answer the specific questions you ask. As stated (5) the sort of treatment envisaged for martian samples is avoided in most geochemical studies. Therefore a series of martian analogues should be subjected to the prescribed treatments and the resulting alteration determined. For example industrial and meteoritic carbides should be examined in light of the sterilization protocol. A small amount of lunar sample should be sacrificed to see how its properties alter with sterilization.

3.

Other martian analogues might be terrestrial basalt, carbonaceous meteorites, etc. With these kinds of experiments it can be determined what sterilization protocols are acceptable and unacceptable.

I regret this little report is so sketchy and provides no hard data, but to me this suggests the need to acquire data to answer your questions. Rest assured that we are very much interested in the subject of returned martian samples and in their analyses. We would like to help in anyway we can to supply information needed at this time or in the future.

Best regards and good luck,

Keith A. Kvenvolden
Chief, Chemical Evolution
Branch

PURDUE UNIVERSITY
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WEST LAFAYETTE, INDIANA 47907

February 27, 1974

Dr. Everett K. Gibson, Jr.
Code TN 7
National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

Thank you for your letter of February 15 regarding questions relevant to the possible return of Martian samples to earth. Before attempting to answer these questions let me give you a little background information regarding some of our recent experiments supported by NASA grant NGL 15-005-140.

As you know, for some years we have been concerned with measuring certain elements, particularly volatile ones, by a combination of neutron activation analysis and atomic absorption spectrometry. The samples studied have been mostly primitive meteorites (i.e. carbonaceous, enstatite and unequilibrated ordinary chondrites) and from the abundance patterns and patterns of interelement relationships we have been examining various models for the formation and evolution of solid material condensed from the solar nebula. About 14 months ago we began a series of investigations dealing with the effects of extended heating of primitive material to simulate thermal metamorphism. Since we had no idea of the possible effects we decided to concentrate upon one primitive meteorite, the C3 chondrite Allende. We have been heating samples of this chondrite in closed systems at 100° increments over a temperature span of 400-1000°C. In most experiments the duration of heating has been arbitrarily set at 1 week (in one case we heated samples at 500°C for 29 days) and the ambient atmosphere has been H_2, initially at $\sim 10^{-5}$ atm (we are currently analyzing separate runs at 1000°C in which O_2 and He were the ambient gases at $\sim 10^{-5}$ atm initially).

In our studies (in some cases in collaboration with others) we are investigating effects of thermal treatment upon: trace element abundances; mineralogy and petrology; stable oxygen isotopic composition; nature of the organic compounds evolved. We are arranging to have the retention of noble gases examined also and to extend these studies to temperatures up to 1500°C when a suitable

reaction vessel is successfully tested. From the trace element standpoint we have been analyzing for Co, Ga, Se, Bi, Tl and In (listed in order of increasing depletion, i.e. presumed volatility, in equilibrated ordinary chondrites relative to Cl chondrites) in both 100 mesh powder and chunks (~5-8 mm) of Allende. We are now extending these studies to other primitive meteorites and will determine an additional 5 elements (Ag, Cs, Te, Zn and Cd) together with the 6 elements listed above.

With that lengthy introduction let me now proceed to the questions you raised.

1. Properties to be measured in returned Martian samples. Clearly a number of important experiments could be suggested and I will enumerate those which I personally feel to be the most important and interesting. It would be desirable to determine all of the chemical elements in each sample. Since this probably cannot be done I would suggest that the following would be the most important: volatile/chalcophile elements - noble gases, halogens, Ag, Bi, C, Cd, Co, Ga, Ge, In, N, Pb, S, Se, Te, Tl, Zn; siderophile elements - Au, Co, Cu, Ir, Ni; lithophile elements - alkali metals, rare earth elements, Al, O, Th, U; major elements - e.g. Ca, Fe, Mg, Mn, Si. It will be essential to investigate the mineralogy and petrology of the samples and their ages. It will also be necessary to investigate the isotopic composition of stable isotopes of C, H, O, Pb and S and it would be useful to determine amounts of molecular gases (e.g. H_2O, CO, CO_2, etc.) present in the samples.

2. Importance of measurements. Determination of the elements listed above should permit establishment of the main Martian geochemical fractionation processes including core formation and mineral formation. Information on volatile/chalcophile and siderophile elements should permit assessment of meteoritic contribution to the Martian surface although weathering effects may complicate the picture. The prevalence of fumaroles should also be indicated by data for these elements. The importance of age determinations (Rb/Sr, Pb/Pb, U, Th/He, K/Ar) are self-evident as are mineralogic and petrographic investigations. Investigation of the composition of stable isotopes of the elements listed may lead to an understanding of the meteorological conditions on Mars and/or the formation temperature of various minerals.

3. Effects of thermal sterilization. Sterilization will affect some of the parameters listed above to a greater or lesser extent depending on the conditions used. From our experiments we know that the retention of Ga, Se, In, Bi and Tl

decreases (in that order) with heating. At 1000° all 5 are lost to some extent while at 400° only Tl is lost (all heating times 1 week) from Allende. We guess that in other primitive samples similar results will occur; we should have further information on this by May 1974. We guess that the other volatile/chalcophile elements listed in answer to question 1 will also be lost by heating; in some cases we will have information on this in May. We know that the mineralogy and petrology of Allende is altered by heating at temperatures $\geq$ 700°C and we guess that such effects would be evident at lower temperatures for such clay minerals as montmorillonite. We guess that the ages of samples would be affected by thermal treatment because of loss of noble gases. We guess that re-equilibration of stable isotopes of C, H, O, Pb and S will occur as a result of sterilization (we should have information on this shortly) and that molecular gas concentrations will also be affected. Naturally carbon-based organic compounds will be affected since that is the purpose of the heating. I guess that magnetic properties and other physical properties (thermoluminescence, etc.) will also be affected by heating.

4. Further research needed. If a decision to proceed is made it would be enormously helpful for a decision to be made on the sterilization mode to be used since this would reduce the number of necessary experiments. From the standpoint of "damage" to the samples I feel that dry heat sterilization in a sealed container at the lowest temperature would be least harmful. If this can be decided upon it will be necessary to conduct experiments on likely geologic samples to assess effects upon the various parameters. As mentioned we will be doing some of these experiments shortly under the aegis of our NASA grant. In addition we presently have a proposal under consideration by the NSF to conduct similar investigations on some terrestrial geologic samples.

I hope that the above is of use to you. If you have any further questions please feel free to ask them and I'll try to answer them promptly. I look forward to seeing your report to the Administrator.

With best regards,

Michael E. Lipschutz
Professor of Chemistry
and Geosciences

cc: Dr. Hosterman, NASA
Dean Andrews, Purdue
Dr. Benkeser, Purdue
Dr. Davis, Purdue

MEL:JJB

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DEPARTMENT OF CHEMISTRY
REVELLE COLLEGE

POST OFFICE BOX 109
LA JOLLA, CALIFORNIA 92037

March 15, 1974

Dr. L. Nyquist, TN7
NASA/Johnson Space Center
Houston, Texas 77058

Dear Larry:

As a follow-up of our telephone conversations, I will summarize below my opinion and recommendations with regard to the type and temperature history of returned samples from the Martian surface.

1. A sample return from Mars requires the consideration of possible biological contamination of Earth by harmful organisms. This question appears to be more appropriate than in the case of lunar sample return.

2. With regard to possible sterilization, I think nobody has any idea as to what kind of organisms have to be considered, and, therefore, it seems to be extremely hard to specify a maximum temperature and time for the sterilization. To be absolutely safe, a very high temperature would be required.

3. A high sterilization temperature would scientifically degrade the Martian samples to a very large degree (this applies to physical, chemical, isotopic properties and others).

4. A minimum of gas phase and gas-solid reactions is obtained if the sterilization is carried out in a sealed container in a vacuum or near-vacuum. Also this makes it possible to analyse the reaction products in the gas phase and also diffused gases.

5. Since the gas phase of a sealed sample container will almost certainly differ from the composition of the Martian atmosphere, a sample of the Martian atmosphere should be taken in a sealed container. I would like to stress the scientific importance of such a sample.

6. Based on the arguments discussed above, I suggest the following scheme of sample return. At least three sealed containers should be returned; two sample containers, one with a sample of the Martian atmosphere. The first sealed sample container should be heated to a high temperature to effectively sterilize the samples.

The second sealed sample container should not be sterilized. A sterilization of the second container, which would be stored in the sealed condition, should be made contingent on the results obtained from the sterilized samples. It is possible that only a mild or no sterilization will be required, therefore maximizing the scientific information available from these samples . I will be glad to discuss any of the above suggestions and others in more detail with you.

Sincerely yours,

Kurt Marti

KM/mis

TO: Dr. Larry Nyquist, TN7
JSC

24 March 1974

FROM: Dr. Kurt Marti

Here are some additional comments on the Martian samples you requested:

7. A biological sterilization would release an unknown percentage of radiogenic, spallogenic and implanted gases. This would, of course, invalidate radiogenic ages and exposure ages based on gas concentrations. On the other hand, ages based on isotopic data of a single element such as ^{39}Ar-^{40}Ar, ^{81}Kr-Kr are expected to be unaffected by sterilization. Information on extinct elements should be extractable, even if the samples have been heated.

8. A sample of atmospheric gases is expected to give important information such as a) composition of early atmosphere, b) solar wind contribution to the Martian atmosphere, c) diffusion of gases into the atmosphere.

9. Sterilization will affect information on regolith dynamics. However, parameters such as hardness of irradiation, neutron effects and shielding can now be obtained from the isotopic composition of heavy rare gases and therefore will be little affected.

XC: K. Marti

INTRODUCTION

In 1965 NASA negotiated a small contract with Bendix Corporation and the University of Michigan to study the effects of the lunar surface environment (mainly the heating and cooling cycle) on certain minerals. The results of this study are summarized in a report to NASA and are given in more detail in a Master's Thesis by Franklin F. Foit, Jr. in the Geology Department at the University of Michigan. As it turned out, the results of this study were not particularly pertinent to lunar minerals (with the possible exception of Geothite) but may be much more applicable to Martian minerals.

The study consisted of two parts. First all available thermodynamic data was used to estimate the stability field of 10 selected minerals under temperature conditions of -180 to +130°C and at high vacuum. Secondly, actual minerals were heated in vacuum in a mass spectrometer and volatile species were monitored as a function of temperature to determine the kinetic stability of each of the 10 mineral groups.

Results

Some of the more pertinent results are as follows:

Goethite decomposes to hematite and H_2O at about 130°C in a matter of minutes at moderate pressures (10^{-6} torr).

Calcite: Under high vacuum (10^{-12} mm Hg of CO_2 pressure), calcite breaks down at about 200°C. However, in short heating runs (~2 hours), calcite did not break down until temperatures of about 500°C were reached.

Calcium montmorillonite: This layer mineral loses its interlayer water under moderate temperatures (100-300°C) at 1 atmosphere. If the mineral is not completely dehydrated, it becomes hygroscopic and readily absorbs water when reexposed. Under moderate vacuum conditions (10^{-5}) considerable water is lost even at 100°C.

Gypsum: At 100°C and 1 atm., gypsum will dehydrate to hemihydrate and at slight vacuum (1 mm) will dehydrate to anhydrate. Under moderate vacuum (10^{-6}) gypsum dehydrates at quite low temperatures $\leq$ 30°C.

Other minerals that may decompose under 200°C vacuum conditions include Serpentine, Natrolite, and possibly actinolite.

SUMMARY: Many common low temperature environment minerals were shown by this study to be unstable at moderate heating under vacuum. It is likely that some of these minerals may be present on Mars and it is equally likely that they would be seriously degraded by the proposed sterilization techniques. A study should be made of the actual effects of these breakdown reactions. This study should include X-ray diffraction on a hot stage and scanning electron microscope observation on a hot stage. Only with this kind of detailed study will all the effects of heating become apparent.

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

IN REPLY REFER TO:

Branch of Isotope Geology

February 27, 1974

Dr. Robin Brett
N. A. S. A.
Johnson Space Center
Houston, Texas 77058

Dear Robin:

Enclosed you will find a short report on the effects of proposed sterilization on charged particle tracks.

I hope this will be helpful to you.

Sincerely,

Charles W. Naeser

1. Materials suitable for charged particle track studies should be present on the Martian surface. Carr (1973) has pointed out a number of features on the Martian surface which are volcanic in origin. Most minerals present in the volcanic deposits are capable of recording charged particle tracks. Probable minerals would be; pyroxenes, feldspars, olivine, and accessory zircon and apatite. Impact events are also common on the Martian surface (Hartmann, 1973). The glass produced during the impact can also be used as a charged particle track recorder. Only montmorillonite, a probable component, would probably not be useful as a track recorder. The expandable nature and fine grain size of montmorillonite make it almost impossible to etch.

2. Studies of charged particle tracks in returned lunar material have provided important information on the history of the lunar surface. Fleischer and others (1971) were able to reconstruct the post crystallization history of rock 12017. This was accomplished by looking at the charged particle track record in pyroxene, feldspar and glass phases that made up this rock. By looking at the tracks in the green glass spherules, Fleischer and Hart (1973) were able to determine that the glass has been at the surface for a relatively short time. Fleischer and others (1970) were able to say that down to a depth of at least 12 cm, the lunar surface is constantly being stirred. This was determined by looking at the fossil track densities in anorthite, glass, and augite grains found in the lunar soil.

3. There is every reason to believe that charged particle track studies on returned Martian samples would provide valuable information. The proposed thermal sterilization of the Martian samples would anneal (erase) the charged particle tracks in some or all of the material depending on the temperature used.

Table 1 shows the approximate temperature at which annealing would begin after a one hour heating.

Table 1

Track reduction would begin after one hour at:

100°C	Basaltic glass	MacDougall, 1973
	Lunar impact glass	Fleischer and others, 1971
200°C	Feldspar glass	Fleischer and others, 1968
	Basaltic glass	Fleischer and others, 1969
300°C	Apatite	Naeser and Faul, 1969
	Lunar impact glass	Fleischer and Hart, 1973
400°C	Phlogopite	Maurette and others, 1964
	Muscovite	Fleischer and others, 1964
500°C	Pyroxene (pidgeonite)	Fleischer and others, 1965a
	Olivine	Fleischer and others, 1965b
600°C	Sphene	Naeser and Faul, 1969
	Epidote	Naeser and others, 1970
700°C	Zircon	Fleischer and others, 1965b
	Feldspar	Fleischer and others, 1965a

Lower temperatures for longer times would have a similar effect. For example, apatite held at 225°C for 10^4 minutes (6.9 days) would also be partly annealed (Naeser and Faul, 1969).

If thermal sterilization must be used on the Martian samples, the lowest possible temperature for the shortest possible time would be best. Incandesence would remove all tracks in all phases present. The higher and higher the temperature, more and more phases will become unsuitable for charge particle track studies.

4. Research is needed on the track retention properties of clay minerals. While it is unlikely that montmorillonite can be etched, some research should be done on it and other clay minerals to determine if any useful track data can be derived from them if they should be present in the returned Martian samples.

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StonyBrook

20 February 1974

Dr. Everett K. Gibson, Jr.
Code TN7
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Gibson:

I am writing in response to your letter of 15 February regarding the scientific results that might be expected from a returned Martian sample. In accord with our prior telephone conversation, I will confine my remarks primarily to those aspects related to the Martian atmosphere.

We will clearly be in a much better position to address this whole question after the Viking missions when we know more about Mars and more about our ability to learn about Mars by means of experiments sent to the planet. Nevertheless, it is already obvious that we can do a much better job of atmospheric analysis on a sample brought to our laboratories than we can hope to achieve with miniaturized instruments sent to Mars. The main problem with sterilization in this area is the chemical reactions that would occur between the solid sample and the atmosphere. We will even be in a better position to assess this problem after Viking, since the heating of samples in ovens for analysis by the GCMS is similar to the sterilization procedures being suggested. Lacking all this vital information, I have attempted to answer the points raised in your letter in fairly general terms.

1. Proposed methods of sterilization

I would prefer dry heat in a sealed container in order to retain all evolved gases and to avoid additional chemical reactions. A helpful addition to this protocol would be an independently gathered and sterilized atmospheric sample that could serve as a control. The temperature regime is harder to evaluate, but the two extremes (a) and (d) are certainly less desirable than (b) or (c). We will have specific information for use in evaluating this question after running the GCMS experiment on Mars.

2. Present knowledge of atmospheric composition

I am enclosing a table from a forthcoming paper (in Comments on Astrophysics and Space Physics) that gives my best current estimate of the relative abundances of gases in the Martian atmosphere. In your informal compilation "Nature of the Martian Surface" there are some errors and redundancies in item 3 that should be clarified by

this table. In particular, it is the mean total (not H_2O) pressure that is 5-6 millibars; the H_2O content is highly variable with season and location on the planet (ranging from < 2 to > 40 precipitable micrometers) and ozone has definitely been detected--also in variable amounts.

3. Properties to be measured in returned sample (gas)

The basic quantities desired are the relative abundances of all constituents, including isotopic forms. We will get a good first cut at this with Viking. To improve on these preliminary results, one will want to use a very high resolution mass spectrometer and/or sophisticated methods of separating constituents (e.g., by gas chromatography) in order to provide better data on ^{20}Ne in the presence of ^{40}Ar (doubly charged in MS), N_2 and CO in each other's presence and in all that CO_2, and other possible mass/charge overlaps that may occur with trace constituents.

Two exciting isotopic problems that are unlikely to be solved by in situ analysis are

D/H in Martian water and
$^{13}C/^{12}C$ in Martian organic compounds.

We may have difficulty with neon and nitrogen isotopes in our initial analysis if these gases are present in very small amounts. Here again a returned sample would help.

Another interesting problem concerns the composition of gases trapped in the rocks. The temperatures achieved in the Viking GCMS ovens will not be high enough to perform this experiment adequately on Mars. We also lack the capability of detecting and measuring gases with molecular weights less than 12. Both of these constraints could be removed with ground-based instrumentation.

4. Significance of measurements for understanding Mars

The role of terrestrial atmospheric studies in the development of our knowledge about the Earth is well known. We expect similar progress to be made with an understanding of the Martian atmosphere, as I have attempted to demonstrate in the enclosed papers.

I hope these remarks are useful; I am certainly interested in the possibility of a returned sample and will be happy to do what I can to support your efforts in this direction. I have passed your letter along to others in our department who may be interested.

With best wishes,

Sincerely,

Toby Owen

Tobias Owen

TO:pm
Encl.

TABLE I

Composition of the Martian Atmosphere

Gas	Abundance (cm am)	Relative Abundance	Reference
CO_2	7500 ± 1000	≥ 900,000 ppm	A
CO	13 ± 8	1,600	B
O_2	9 ± 2	1,100	C
H_2O*	2.5 ± 1.5	300	D
O_3*	2.5 ± 1.5 x 10^{-4}	0.03	E

*These constituents are known to vary with seasonal and diurnal cycles.

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C-3

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March 13, 1974

Dr. William Phinney
Chief, Geology Branch
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Bill:

Reference is made to your February 19th communication, concerning the degree to which studies of a Martian sample will be compromised by the proposed sterilization procedures. We will not remark in detail on the effect of heating to temperatures of 350°C on such minerals as hydrous iron oxides, carbonates, hydroxides, etc. Others have given input to you on these minerals. We will only add that even if the sterilization procedure tends to dehydrate or oxidize some of these minerals, most important crystal chemical information should remain intact and an accurate prediction of the nature of these minerals on the Martian surface should be possible.

Most of our work to date has been on silicates such as amphiboles, pyroxenes, feldspars, etc., and the Fe-Mg-Ti oxides, and these phases are likely to occur on Mars. We will be especially interested in the nature of these phases when they occur in Martian volcanic rocks. Our studies will concern the near surface chemical and thermal evolution of these rocks and after selecting candidates for primary liquids, we will address the problem of their source regions. It is likely that these rocks will already be compromised (weathered) by exposure to the CO_2-rich Martian atmosphere. However, we should be able to see through this alteration overprint and determine the character and petrogenetic history of these rocks. It is unlikely that reasonable sterilization treatment ($T < 350°C$, inert atmosphere) will compromise these rocks significantly. Judicious choice of an inert atmosphere (e.g., N_2) is particularly important. We do not believe that other accepted sterilization techniques (e.g., infrared radiation) would compromise the samples seriously. In summary, I would state that the important (at least to us) petrologic aspects of origin of Mars such as the nature of the crust, genesis of volcanic rocks and the nature of the Martian interior will not be unduly compromised by the proposed sterilization procedures. On the

other hand, clues to the details of Martian surface weathering and alteration could be greatly obscured by any sterilization procedure which dehydrates or changes the oxidation state of iron in the low-temperature mineral assemblages. However, we repeat, the basic petrologic information concerned with planetary formation and differentiation will probably still be intact.

Sincerely yours,

JJP;AEB:sk

J. J. Papike

A. E. Bence

CALIFORNIA INSTITUTE OF TECHNOLOGY

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DIVISION OF GEOLOGICAL
AND PLANETARY SCIENCES

TELEPHONE (213) 795-6811

March 7, 1974
RE: TN7

Dr. Laurence E. Nyquist
National Aeronautics and
Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Dr. Nyquist:

The chemical composition and molecular structure of most nitrogenous, carbonaceous, and hydrated substances in the Martian samples would probably be seriously altered by temperatures substantially above 25°C. Heat treatment of the samples would probably negate most chemical measurements bearing on surface chemical conditions of Mars by forming, in the samples, compounds that did not exist on Mars and destroying many of those that did. The comments that follow do not deal with the above problems at all, but relate instead to the effects of heat treatment on the trace metal composition of the samples, with particular reference to lead.

Great care must be exercised to minimize trace metal impurities of the metals or plastics used in the sample collecting apparatus, together with trace metal contaminations of the surfaces of these materials from the time they have been cleaned to the time they are used to collect a sample.

I won't go into details about this matter here. It is sufficient to say that the steps that must be taken to control heavy metal contamination on a reliable basis are both unbelievable and incomprehensible to engineers and scientists outside this restricted field of study, and it is not possible to set down instructions and advice for controlling contamination which engineers and scientists outside the field can use. Even after procedures for construction and assembly have been worked out, a scientist used to working at ultra low levels of heavy metal contamination must supervise the entire operation from fabrication to liftoff, in order to insure optimum contamination control.

Two substances that have been proven by bloody experience to be most trustworthy with respect to trace metal contamination are (1) fused quartz made from ultra fine grade crystals, with the stock being handled during fabrication with new, clean graphite tools, with the quartz subsequently being cleaned successively with HF, HNO_3, and ultra pure acidified water; and (2) FEP teflon in fabricated form being boiled with prolonged, successive treatments of pure aqua regia, HNO_3, and ultra pure slightly acidified water. It is probable that the use of other substances, such as

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stainless steel, TFE teflon, or polyethylene for materials that would contact the Mars samples would introduce sufficient amounts of trace metal contamination to substantially degrade the scientific integrity of the samples.

A fused quartz liner could be heated up to 350°C without damage. FEP teflon could only be heated safely to 150°C for a month, with higher temperatures being unsafe.

There are two serious drawbacks to heating the samples: (1) volatile metallic substances may be driven out of the samples and lost; and (2) volatile metallic contamination, originating from heated materials outside the sample container lining, may be carried inside the sample container. The probability of both of these effects operating at significant levels is high enough, by themselves, to seriously compromise the scientific integrity of the samples.

It should be clear that geochemists look with horror on heating their samples, and for valid reason.

Sincerely,

C. C. Patterson

CCP:bac

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DEPARTMENT OF PHYSICS

BERKELEY, CALIFORNIA 94720

February 22, 1974

Robin Brett
Code TN7
NASA Johnson Space Center
Houston, Texas 77058

Dear Robin:

I am responding to your letter of February 15, 1974, concerning the effects of sterilization on Mars samples.

1. Track studies that could be carried out on Mars samples.

The present Martian atmosphere shields surface soil grains from all but the penetrating cosmic rays - in the case of Fe nuclei such as are responsible for the majority of tracks in lunar samples, energies must be higher than ~500 MeV/nucleon. Amorphous coatings on grains due to solar wind irradiation will be absent. Microerosion and mass wastage erosion will be absent. Track densities will be much lower than in lunar grains. Fission track dating will be easy, with such a drastically reduced track background. One ought to be able to determine absolute solidification ages of very small samples without having to search for the rare, uranium-rich phases. Paleovolcanism and soil transport could be studied by fission track dating of individual grains.

One could search for rare grains with steep gradients, which, if found, must have been produced when there was no Martian atmosphere. Contamination of the soil by fragments of gas-rich meteorites could also contribute, but could be distinguished from indigenous grains.

I am sure that several minutes more thought could turn up other interesting problems that can be tackled by track techniques.

2. Effects of sterilization on tracks

a) "Clay" minerals. Not much is known. Assuming mica to be a representative layer-lattice silicate, we can say that 150°C for 1 month would have no effect, but that 250°C for 1 week or 300°-350°C for 1 day might cause some fading of tracks.

b) Basaltic minerals. Very track-retentive minerals such as sphene, zircon, diopside, garnet and some feldspars can stand temperatures up to ~600 or even 700°C for 1 hour and perhaps 100° lower temperatures for 1 month. Less retentive minerals such as apatite, whitlockite and olivine will begin to lose tracks at temperatures as low as 400°C in 1 hour.

Yours sincerely,

Buford

P. Buford Price

PBP:mk

U of C-AUA-USAEC

ARGONNE NATIONAL LABORATORY

8 March 1974

Dr. Everett K. Gibson, Jr.
ATTN: TN7
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Everett:

We recommend that the biological sterilization of Mars samples be restricted to either ambient temperature ethylene oxide treatment or to dry or wet heat limited to 150°C in a closed system. Our rationale is as follows.

Several elements and compounds must be considered as volcanic emanations and/or weathering products: (1) highly volatile reactive agents such as H_2O, HCl, HBr, HF, and H_2S; (2) highly volatile non-reactive elements such as Hg and the rare gases and (3) moderately volatile, relatively non-reactive elements (compounds) such as Pb, Bi, Tl and Os.

Stepwise heating and aqueous leaching experiments on lunar samples have established that a number of elements, which terrestrially may be associated with fumarolic activity, are present on surfaces. All of the halogens in lunar samples, except possibly F, are mobile. Some Br is volatilized at 150°C; leaching experiments for I and release of ^{128}Xe (produced from I) at low temperatures indicate that I will also volatilize. The element Hg is possibly one of the most abundant volatiles on the lunar surface and must be present as a component of the atmosphere at lunar day time temperatures. Pb can be leached at pH 5-6 and volatilized at temperatures as low as 450°C.

Since these elements will provide important information of Martian vulcanism and surface weathering processes, the samples should be compromised as little as possible. We suggest that: (1) both sterilization procedures be employed assuming that at least two sample containers will be returned. This should satisfy both organic and inorganic interests; (2) the ethylene oxide treated samples should not be heated; (3) the heat treated samples should be maintained at temperatures of <150°C. If wet-heat is recommended

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then deuterated H_2O should be used. The atmosphere of the container should not be vented to space but be maintained intact for tapping at the receiving laboratory and (4) obviously, containers and reagents should be selected for freedom from contaminants and should be passive to possible compounds released during the sterilization process, for instance HCl.

Sincerely,

George W. Reed, Jr.
Chemistry Division

GWR/ljc

The following information was supplied by

Dr. R. C. Reedy
Los Alamos Scientific Laboratory
of the University of California
Los Alamos, New Mexico

in response to a question regarding the expected production rates of certain nuclides by cosmic-ray interactions in the Martian atmosphere. The production rates are based on calculations used in the paper "Interaction of Solar and Galactic Cosmic Ray Particles with the Moon" by R. C. Reedy and J. R. Arnold (Jour. of Geophys. Res., 77, pp. 537-555, 1972). The cosmic ray fluxes used are the values at 1 A.U. These fluxes will not be drastically different at the Martian orbit for galactic cosmic rays, the only ones considered here. Permission to include the following information in this report was verbally given by R. C. Reedy to L. E. Nyquist. The original notes were transcribed by L. E. Nyquist, any errors in transcription are his.

I. Productuion rate by galactic cosmic rays in 100% CO_2 atmosphere (atoms/min per kg of oxygen).

Depth (g/cm^2)	0	20	40
^{3}H	203	206	191
^{10}Be	16	17	16
^{14}C	34	48	52

II. Neutron capture production of ^{14}C from ^{14}N.

i. 95.8% of total captures in ^{14}N produce ^{14}C.

ii. 5% N captures 98.9% of total neutrons in a 95% CO_2 (by weight) atmosphere.

iii. 0.5% N captures 89.5% of total neutrons in a 99.5% CO_2 atmosphere.

iv. Using the Lingenfelter, Canfield, and Hempel Model (Earth Planet. Sci. Lett. 16, 355, 1972) for neutron production yields the following capture and production rates:

Depth (g/cm^2)	LCH captures / kg min	atoms ^{14}C / kg min (5% N)	atoms ^{14}C / kg min (0.5% N)
0	120	51	5.1
5	225	96	9.6
10	327	139	14.0
20	516	220	22.0

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DEPARTMENT OF PHYSICS

BERKELEY, CALIFORNIA 94720

March 8, 1974

Dr. Laurence E. Nyquist
Code TN-7
NASA Johnson Space Center
Houston, Texas 77058

Dear Larry:

As usual these days I am late in replying and even so have not spent the time on this that it deserves. Thus you are getting an off-the-top-of-the-head answer and I am reasonably sure that everything I have said here will have been anticipated by you.

From the standpoint of rare gas research I think it is clear that a temperature run of irradiated and unirradiated material maximizes the possible information obtained. One gets from these experiments an Argon-39/Argon-40 age for almost anything, possible xenon from extinct radioactivities, indications whether this xenon from extinct radioactivities was produced in situ or not, information about the trapped rare gases in the sample, certain of the trace elements - namely Br, I, Ba, U, exposure ages from the $^{81}Kr^{80}Kr$ relationships and from the ^{38}Ar-Ca relationships.

It is also obvious that the lowest temperature sterilization among your proposed regimes is the most favorable from the standpoint of the rare gas analyses. In almost any sample the long low temperature heating will release less gas than the shorter high temperature heating. If there is a choice to be made between heating the sample in a closed container or in vacuum it would be better from the standpoint of rare gas research to heat it in a closed container. The gases driven off can then be examined. It is important to have a sample of the Martian atmosphere as well but if possible this ought to be a separate sample, not mixed with the gases released in the sterilization. By the same token it would be better if the sample, or at least part of it, were evacuated before the sterilization process began.

I hope this information is of some use to you. Clearly the detailed design of an experiment would require knowing all the various limitations on the sample and the uses to be made of the sample.

Sincerely yours,

John H. Reynolds
Professor of Physics

JHR/ek

Motoaki Sato
U.S. Geological Survey

This is in reply to your inquiry on the possible effects of biological sterilization on returned Martian samples. The questions asked are so sweepingly broad and time to answer is so short that I feel a little uneasy about making written statements, but in view of urgent circumstances you described, I will jot down whatever that have come up in my mind at a risk of mixing up speculations with facts and established principles.

1. The properties that should be measured or studied within the realm of petrology and geochemistry are as follows:
   i) Mineral assemblages and textural relations.
   ii) Major and trace element composition.
   iii) Oxidation state (Fe^{3+}/Fe^{2+} ratio and intrinsic oxygen fugacities).
   iv) Composition of volatiles.
2. The reason for studying the above properties are briefly described below in the same sequence.
   i) Minerals, singly and in assemblage, reflect the chemical and physical factors of various environments they have been exposed to. Regardless of whether a sample is an igneous rock, soil or something else, detailed examination of individual minerals and mineral assemblages tells us a lot, needless to say.
   ii) This is more or less routine and one of the first things one would try to find out.
   iii) The state of oxidation of Martian rocks is a subject of more than passing interest. It will probably give us a strong clue as to the mechanism of control of the oxidation state of igneous rocks on various planets. The reddish albedo of Martian soil

or lavas, which is believed to be due to ferric iron on the basis of spectral correspondence, may be produced in four different ways.

The first possible way is oxidation by atmospheric free oxygen similar to the formation of lateritic soils on Earth. This mechanism would require the presence of photo-synthetic plants or bacteria to liberate free oxygen from carbon dioxide and water, if the Martian magmas were similar to terrestrial or lunar magmas. The gases extracted from deep sea pillow basalts at high temperatures exclude the possibility of presence of free oxygen at equilibrium (Sato et. al. unpublished data). Oxygen fugacity values of relatively uncontaminated magmatic gases are significantly below that of the hematite-magnetite assemblage (Sato and Wright 1966, Sato and Moore 1972).

The second alternative is that the Martian interior was extremely rich in oxygen and the Martian magmas were oxidized from the start, and as the result hematite or other high ferric minerals crystallized directly out of magma as primary igneous minerals. This mechanism would require an extraordinary setting for the origin of Mars. The cosmic elemental abundance favors reduced states for iron at high temperatures. Iron in chondrites occur in reduced states.

The third alternative is that magnetite was attacked by CO_2-rich water and reacted to form hematite (or ferric hydroxide) and siderite:

$$Fe_3O_4 + CO_2 = Fe_2O_3 + FeCO_3 \quad \Delta F^\circ_{298} = -1.50 \text{ Kcal} \qquad (1)$$

$$Fe_3O_4 + CO_{2(g)} + 3H_2O_{(\ell)} = 2\,Fe(OH)_3 + FeCO_3 \quad \Delta F^\circ_{298} = +3.67 \text{ Kcal} \qquad (2)$$

The free energies of reaction were computed on the basis of data in Latimer (1952), except for $Fe(OH)_3$ which is based on JANAF (1971). Reaction (1) requires partial pressure of CO_2 greater than 80 mb at 25°C to proceed. Reaction (2) should have more negative free energy of reaction

than (2), considering the reported observation that goethite is more stable than hematite at activity of water greater than 0.6 (Schmalz, 1956). Unfortunately, only values for unstable $Fe(OH)_3$ are found in standard reference sources. The reaction is within the realm of possibility on Mars.

The fourth alternative is that the oxidation was caused by preferential escape of hydrogen originated by the thermal dissociation of water in the late magmatic to duteric stage. Formation of ferric oxide probably due to this mechanism was observed and described in Hawaii (Sato and Wright 1966) and elsewhere. There are other pieces of evidence which suggest that oxidation by this mechanism is prevalent in magmas which contain water. Sato et. al. (1973) pointed out a possibility that the difference in the oxidation state between terrestrial and lunar igneous rocks is due primarily to the difference in the initial water content of magma, which in turn is due to the difference in total mass between the two planets. The smaller Moon lost much of water (a light-weight molecule) at the time of formation because of its small gravitational field, whereas the larger Earth retained a considerable amount of water.

The oxidation state of the Martian rocks is of extreme interest because the mass of this planet and probably the water content fall between the Earth and the Moon. The escape of hydrogen would be easier if a planet is smaller. On the other hand, the internal water content would be less if a planet is smaller, as discussed earlier. It may turn out that Mars represents the optimum planetary size for the oxidation of magma by hydrogen loss.

The intrinsic oxygen fugacities of mafic minerals indicate the course of change in oxidation state of a magma (Sato 1972).

Terrestrial basalts show a tendency of increasing oxidation with decreasing depth (Sato unpublished data), whereas lunar basalts show an opposite tendency (Sato et. al. 1973). Examination of the intrinsic oxygen fugacities of Martian igneous minerals would show which way the oxidation state of Martian magma changes with depth (or at least with the degree of crystallization). This information would most likely to be a crucial clue to the understanding of the mechanism of control of the oxidation state of magmas in the Solar planets.

iv) The composition of volatiles in any rock is an important information to obtain. Volatile compounds control the origin of atmosphere, hydrosphere and life. Photosynthesis requires the availability of CO_2 and H_2O to produce high-energy compounds such as carbohydrates. Without these photosynthetic products, higher organisms may not operate.

Volatiles also play an important role in controlling the oxidation state of igneous and metamorphic rocks as partly pointed out by Sato et. al. (1973). Volcanic activities depend heavily on the volatile components in magma. Explosive volcanic eruptions and ash falls would not occur without volatiles. Geothermal heat transfer would be very ineffective without volatiles. Valuable mineral deposits may not form without them.

3. Sterilization is simply undesirable for any measurements mentioned above except possibly category (ii) (chemical composition). It would be ideal if the samples are returned to a Sky-Lab type space station first for biological testing and quarantine for 3 months or so, and then shipped intact to the Earth receiving lab. The samples need be quarantined regardless of whether they are sterilized or not, because nobody

could possibly be sure that a certain sterilization procedure is foolproof, except perhaps (d) heating to incandescence, a procedure which would destroy practically all useful information for which the samples will be brought back. This procedure would probably not destroy the bulk chemical composition, but for that there would be no need to bring the samples back. Just send an analyzer to Mars.

If we have to live with sterilization, procedures (a) and (c) must be rejected. Heating in vacuum would result in loss of volatiles, resulting in oxidation or reduction of samples, dehydration or decarbonation of hydrous minerals and carbonates, and change in volatile composition, as discussed earlier. Addition of water would obliterate information on volatile contents and degree of hydration of minerals. The presence of water vapor also tends to accelerate reactions among co-existing phases and thus likely to obliterate the memory of Martian environments locked in minerals. It does not make sense to deliberately help erase valuable recording of the Martian environment and substitute it with a recording of the environment in the sterilization chamber, even for 18 1/2 minutes!

The only procedure reluctantly acceptable is (b) dry heat sterilization in a sealed gold container. No base or ferrous metal container would be acceptable because of possible reaction with the sample. Platinum group metals are not acceptable because they are permeable to hydrogen.

Should water vapor exist in the sample, the rise in vapor pressure would result in hydrogen osmosis and resultant change in volatile composition and oxidation of the sample. This would be particularly so if the container is exposed to the high vacuum of space. Single crystal sapphire container may be acceptable as an alternative to gold.

The times and temperatures should be in such a combination that the reactions within a sample should be minimal. Natural samples are normally disequilibrium assemblages at any temperature. That is why we can decipher their geologic histories by carefully studying them. Now if we assume that a reaction is a first-order reaction and proceeds at a rate of k, the amount of change that would occur, χ, in time t is:

$$\chi = a(1 - e^{-kt}) \qquad (3)$$

where a is the initial concentration. The rate constant k is a function of absolute temperature:

$$k = Ae^{-Ea/RT} \qquad (4)$$

where A is a constant and Ea the activation energy of the reaction. From (3) and (4), it can be seen that the amount of change that would occur during the sterilization will be the smallest if the temperature-time combination is such that the quantity, $e^{-(Ea/RT)} \cdot t$, is the smallest. The relative values of this quantity depend on the magnitude of the activation energy as shown in Table 1.

Table 1. Relative amounts of reaction that would occur for given temperature-time combinations.

	Temperature (°C)	Time (Days)	Ea (Kcal) 2	5	10	20	50
(a)	150	30	1	1	1	1	1
(b)	250	7	.368	.728	2.27	22.08	2.03×10^{4}
(c)	350	1	.072	.225	1.52	69.25	7.94×10^{41}

The table indicates that if the activation energy is low, a combination of higher temperature and shorter time would produce a relatively smaller amounts of reaction, and vice versa. Gaseous reactions

between stable molecules have values of Ea ranging from 2.5 to over 40 Kcal/mole, and reactions between ions and neutral molecules from 9 to 23 Kcal/mole (Frost and Pearson, 1953). Reactions in solid bodies range from 12 to 180 Kcal/mole (Budnikov and Ginstling, 1968). The majority of these inorganic reactions have activation energies around 20 Kcal/mole or higher. Therefore, combination (a) (low temperature and longer duration) is obviously the best sterilization plan to preserve inorganic disequilibrium relations of Martian samples. We can hope that organic reactions with low activation energies (life processes) reach equilibrium state(dead state), while inorganic record is still preserved through this sterilization procedure.

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March 4, 1974

Dr. Everett K. Gibson, Jr.
TN7
NASA/JSC
Houston, TX 77058

Dear Everett:

Dr. Laul and I cannot add much new information that you are not already familiar with concerning the present state of volatility studies with a variety of elements. You and Norm have essentially done the classic experiments that should be helpful as significant background data for the Martian sample protocols.

We can only emphasize the extreme importance of complete measurements of the entire chemical composition of both bulk and separated "minerals" on such returned samples. Such measurements are basic to all other proposed experiments on these samples. It seems doubtful whether large fractions of many volatiles will be lost for the 150°C and 200-250°C sterilizations. Certainly no lithophiles or refractories will be lost in heating even up to 350°C for one day. However, it seems probable that appreciable fractions of trace elements such as Tl might be lost at 350°C.

We would be willing to participate in a detailed study of volatile bulk and trace elements loss in a variety of samples that might approximate hypothesized Martian soil. See our latest Ap 17 boulder-2 papers for a list of elements. It seems pointless to invest any time in the analyses of refractory bulk and trace elements in such samples, since these elements will not be lost. May I suggest that the sample load for analyses of these volatile elements be shared by the Anders, Wasson and our group or any other group that has such capability.

Best regards,

R. A. Schmitt
Professor of Chemistry

jmw

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DEPARTMENT OF GEOLOGY
LOS ANGELES, CALIFORNIA 90024

March 11, 1974

Dr. William C. Phinney
NASA - L.B.J. Space Center
Houston, Texas 77058
Code: TN7

Dear Dr. Phinney:

In response to your letter of 19 February, the following are opinions (guesses) only, supported by some experience but not by a great deal of data. Obviously, properly designed experiments must be performed to agument and extend the limited data currently available.

1. Properties to be measured.

Clearly, measurement of various physical properties (water content, mineralogy, etc., etc.) will be important. Depending on sterilization regime, such properties can be preserved, and measured, relatively easily.

It is at least equally important -- and in my opinion, absolutely imperative -- that attempts be made to detect evidence of biologic organization. Severe sterilization regimes (e.g. "heating to incandescence"/sic./) will destroy such evidence and, thus, must be avoided. However, less severe regimes (relatively low temperatures for relatively long periods of time) can be employed which will have the desired sterilization effects while, at the same time, preserving the morphology and some biochemistry of hypothetical Martian microbes. In short, the desired goal should be one of providing sufficient energy of activation to break important organic bonds (e.g., C-C bonds, in straight-chain hydrocarbons about 58,000 cal/mole; ABELSON, 1959), and thus kill whatever organisms may be present, while at the same time not destroying the physical form of such organisms. Evidence of such organisms, whether recently dead or fossil, should be sought using "usual" paleobiologic techniques (optical and electron microscopy of powdered preparations, thin sections, acid-resistant organic residues, etc.)

2. Importance.

The "probability" of living systems occurring on Mars, now or in the geologic past of that planet, appears low (although it must be recognized that "probability statements" of this type

are very nearly meaningless since they presuppose the existence of substantive knowledge that is not, in fact, available, knowledge relating to such matters as (i) conditions, processes and events required for the origin of living systems; (ii) the nature of the primitive Martian environment and the evolution of that environment over geologic time; (iii) the evolutionary flexibility and adaptability of biologic systems; etc.) Nevertheless, it is obvious that the discovery of firm evidence of the present or past existence of living systems on Mars, and the characterization of such life forms, would be of tremendous significance. Every effort should be made to avoid the destruction, during sterilization, of possible evidence of Martian life.

3. Potential effect of sterilization.

Paleobotanists, palynologists and coal petrographers have long recognized that both the fidelity of cellular preservation and the color of carbonaceous plant fossils and particulate organic matter ("kerogen") preserved in ancient sediments vary as a function of metamorphic history and degree of coalification. Both in laboratory studies and in nature, a continuum of irreversible color changes (generally from yellow, through shades of amber, reddish brown and brown, to black) occurs during very low grade "metamorphic" alteration of carbonaceous material; temperatures extrapolated from known geothermal gradients or measured in boreholes or in laboratory heating experiments have been correlated with the color of preserved palynomorphs to yield "thermal alteration indices" (for a summary of these indices, see OEHLER, AIZENSHTAT & SCHOPF, 1974) which, in turn, have been used for mapping the distribution of eometamorphic facies and for predicting the potential gas and oil productivity of fossiliferous strata (e.g., GUTJAHR, 1966; STAPLIN, 1969; BURGESS, 1970; CORREIA, 1971; WILSON, 1971; TEICHMUELLER, 1971). Contrary to some reports, it has recently been established (OEHLER, AIZENSHTAT & SCHOPF, 1974) that these changes in color and fidelity of cellular preservation are dependent on both time and temperature -- the same transformations that occur at relatively low temperatures and long periods of time (e.g., 150°C, 2000 hr) also occur in shorter periods of time at higher temperatures (e.g., 300°C, 0.5 hr); the changes are accompanied by increases in C/H ratios, in the percent of fixed carbon, and in the degree of aromatization of the preserved organic matter and alteration occurs more rapidly in the presence of oxygen than under anoxic conditions (OEHLER, AIZENSHTAT & SCHOPF, 1974).

Based on the limited data available on alteration of modern plant material (pollen, spores, and one microorganism -- the blue-green alga Lyngbya), and on observations of preserved microorganisms in ancient sediments, I would evaluate the four suggested sterilization regimes as follows:

(a) 150°C, 30 days (1.3×10^6 secs)

Anoxic: modern microorganisms would be structurally well preserved, fairly easily detectable (especially if stained with appropriate dyes), and would retain a considerable degree of intracellular organization (e.g., membranes, organelles, etc., would be relatively well preserved).

Oxygenic: preservation would be roughly comparable to that under anoxic conditions but alteration would be somewhat greater and dyes would be less useful for detection of microorganisms.

Fossils would be unchanged under this regime.

(b) 200°C, 7 days (3×10^5 secs)

Anoxic: modern microorganisms would be structurally degraded but still identifiable; intracellular organization would be very largely destroyed.

Oxygenic: more degraded (but still identifiable) than under anoxic conditions.

Fossils would be largely unaffected (depending on their mode of preservation and the nature of the surrounding matrix).

(c) 300-350°C, 1 day (4.3×10^4 secs)

Anoxic: modern microorganisms very largely destroyed, probably not identifiable.

Oxygenic: modern microorganisms destroyed, not identifiable.

Fossils probably somewhat altered, but may still be identifiable.

(d) incandescence, 10^2-10^3 secs

All conditions: organic matter volatilized, evidence lost.

Please note that the above are largely guesses; few hard data are available.

4. Further research.

Only one, reasonably applicable study has been published (OEHLER, AIZENSHTAT, & SCHOPF, 1974). This study, of one modern alga, is the only published report of the effect of time-temperature relationships in the degradation of the morphology and biochemistry of a modern microorganism of which I am aware. Clearly, extension of this work -- including investigations of the chemical changes involved and the possible effect of mineral-organic interactions -- is needed. Techniques should be designed to facilitate detection of dead microorganisms following sterilization (e.g., staining

procedures). Alteration of intracellular organization should be monitored by transmission electron microscopic studies. And, studies will be needed to define the effect of the sterilization procedure on fossils, as well as on representative modern microorganisms (it should be noted that studies of this sort, if appropriate modern ~~are~~ chosen, can have applicability to geologic problems -- e.g., the mapping of eometamorphic facies in petroleum exploration -- so that the research performed could have much broader applicability than solely the matter of looking for Martian "bugs").

I hope all this is of some help to you. Please let me know if you have any further questions (213-825-1170).

Sincerely,

Bill Schopf

J. William Schopf
Professor of Geology

References:

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DEPARTMENT OF GEOLOGY AND GEOPHYSICS

Box 2161, Yale Station

March 4, 1974

Dr. Robin Brett
NASA - Johnson Space Center
Houston, Texas 77058

Dear Robin:

Your letter of February 15th concerning the effects of sterilizing procedures on Martian samples opens a complex bag of worms. I can address myself to the effect of heat on three probable kinds of materials to be encountered in the samples:

1) sulfide compounds present as primary minerals
2) condensed sublimates from volcanic processes
3) materials deposited as efflorescences in the Martian.

In addition to these classes of materials I can forsee vast problems associated with any clays, hydroxides, sulfates and similar materials that have formed by surficial alteration, but I presume you have sought advice other than my own on such problems.

1. Sulfides. All igneous rocks contain sulfide minerals and considering the geochemical abundance of sulfur, Martian rocks must be expected to do the same.

The most likely sulfides, regardless of primary igneous or secondary origins, are those of iron and copper. The likely mineral species, in order of probable abundance, are pyrrhotite, chalcopyrite, bornite and chalcocite. It is clear from the attached diagram (Fig. 1) taken from Barton and Skinner (1967), ("Sulfide Mineral Stabilities" in Geochemistry of Hydrothermal Ore Deposits, edited by H. L. Barnes, published by Holt, Rinehart and Winston) that all of the proposed sterilization heating times will produce reactions in sulfides and that for options at 200°C or higher, the reactions will probably proceed to completion and will obliterate most evidence contained within the minerals. The kinds of evidence to be anticipated are cooling rates of primary igneous rocks and because sulfides are the most sensitive group of primary minerals to secondary reactions, evidence of atmosphere induced chemical weathering.

The questions of closed versus open containers and humid versus dry atmospheres is obvious in the case of sulfides. Any heating in the presence of water vapor will produce reactions to form hydroxides and possibly oxides.

Vapor pressures will depend on the mineral species present. Figure 2, also taken from Barton and Skinner, shows that the assemblage pyrrhotite-iron (commonly seen in lunar rocks) would generate such a low sulfur pressure that even up to 300°C, sulfur loss would be small in an open container. However, if pyrrhotite coexisted with pyrite, the vapor pressure of S_2 would be about 10^{-12} atm. at 300°C and we would have to anticipate a significant loss of sulfur in a sample heated for an hour or more. Any heating should therefore be in a closed container.

The most vital information lost by either vapor loss or mineralogical reactions would probably be isotopic. This could be of two kinds. Small fractionations can be anticipated from a variety of inorganic processes such as fumarolic outgassing of volcanoes and atmosphere-rock interactions. If primitive life forms have or do exist on Mars, they may have given rise to sulfur isotope fractionations analogous to those on Earth. Soil and primary rock samples may have large differences in their isotopic ratios as a consequence.

The lower the temperature, the less drastic will be the degradation of sulfide minerals. Of the choices offered, clearly a temperature below 150°C for a month is preferable. A temperature of 100°C would be below most phase inversions and would reduce both reaction rates and vapor pressures to manageable levels. The difference between 100° and 150°C is particularly apparent from Figure 1. It is the difference between little change and drastic changes if copper-bearing minerals are present.

2. Condensed sublimates. Two kinds of materials can be anticipated. If volcanic processes on Mars cause permafrost water to be melted, then sublimates formed by reactions between water and hot magmatic rocks must be anticipated. These materials are common in and around volcanoes and volcanic fields on Earth, but they only persist for a short time because they are soluble and removed by rain. On Mars they would presumably remain and might become soil constituents by physical erosion processes. The kinds of materials likely to be present are gypsum ($CaSO_4 \cdot 2H_2O$) and the hydrous sulfates of iron and aluminum.

The second kind of sublimate is material given off by magmas and the most likely substances are native sulfur, sodium, calcium and iron chlorides.

Regardless of origin, the sublimates will all be influenced by the proposed heatings. The hydrous compounds would all dehydrate, at least partially, and native sulfur would melt. The only species that would be little influenced would be sodium chloride.

All compounds would react with water vapor of an 80% humid atmosphere and all have sufficient vapor pressures so that heating in an open container would lead to a partial or total loss of the material. Sulfur would be particularly vulnerable.

3. Efflorescences. If water or liquid carbon dioxide move in the Martian crust, the question of surface efflorescences arising from their evaporation and consequent precipitation of dissolved materials must be considered as a possibility. An analogy on Earth is the Atacama Desert with its carbonate, nitrate and halide efflorescences. In the case of Mars, nitrates are unlikely, but carbonates and halides must be considered possible. Presumably compounds of the most abundant elements are the most likely salts, so that Na_2CO_3, $CaCO_3$, NaCl, $CaCl_2$, $MgCl_2$ and similar compounds can be anticipated.

Heating in a humid atmosphere would cause a near total disintegration of all compounds except $CaCO_3$. Dry heating in a sealed container should not cause much change provided the temperature did not exceed 100°C. If the salts were present in their hydrated forms, however, even heating at 100°C would lead to release of water.

It seems to me that the "importance of each of these properties", as your letter states, is self-evident. We are dealing with materials that have been degraded physically and chemically on the surface of a planet at temperatures no greater than 25°C. Heating at any temperature will cause degradation products to react with each other and with more abundant rock and soil particles. Heating will also produce vapors containing S, H_2O and CO_2 as a result of mineral breakdowns and reactions. The sulfide minerals are in pretty good shape as far as our understanding of them is concerned. The same cannot be said for many of the possible sublimate and efflorescence compounds and I believe further work on their stabilities and interactions is indicated. Work should involve both isotopic chemistry and mineralogy.

I hope these remarks help you. Given more time I suspect I could have produced a more literate and better documented report.

Kind regards,

Brian J. Skinner

BJS/pk

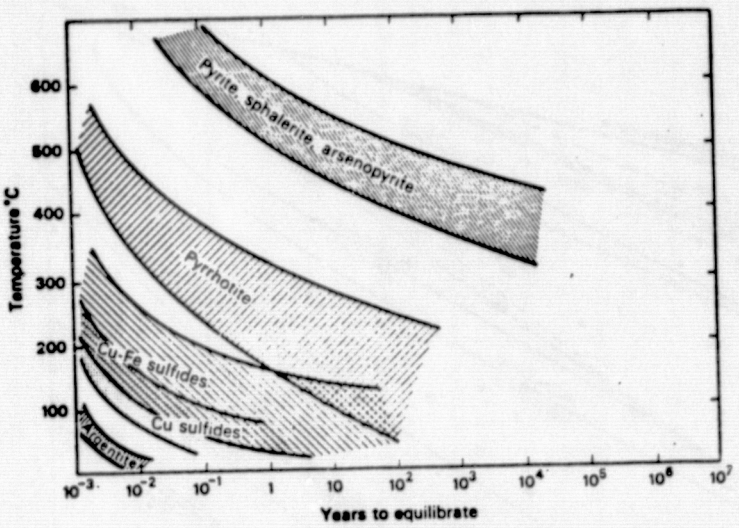


Fig. 7.1. Equilibration times for various sulfides involved in solid-state reactions. The field widths reflect differing rates in different reactions as well as changes due to compositional differences.

Figure 1.

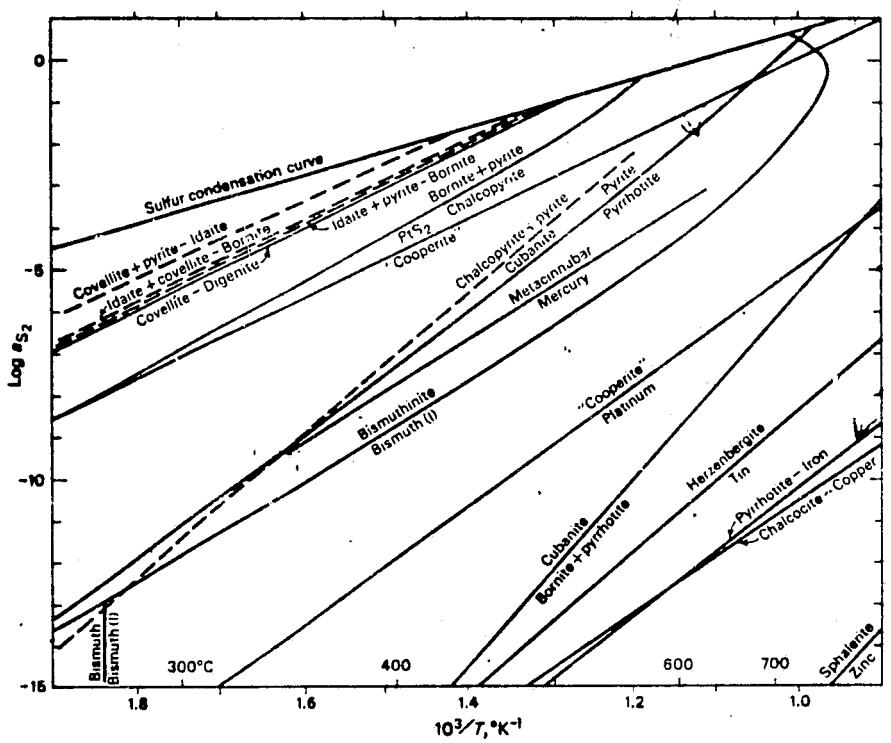


Fig. 7.19. Activity of S_2-temperature diagram for selected sulfidation reactions. Data from which the curves are drawn are presented in Table 7.2. Additional curves have been given in Figs. 7.20 and 7.21. Mineral names are used whenever possible and are enclosed in quotes when the mineralogical identity of the compound is uncertain. Formulas are used for phases that are not known to exist in nature. A minus sign preceeding a phase indicates that the phase is stable below the curve.

Figure 2.

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5734 SOUTH ELLIS AVENUE
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February 21, 1974

Dr. W. C. Phinney
NASA-JSC
Houston, Texas 77058

Dear Bill:

Here are our quick and dirty thoughts on heating the Mars sample to 275° C for one month. Input was provided by J. R. Goldsmith, A. T. Anderson and I. M. Steele.

Serious damage would occur for various types of minerals, but many would survive untouched. The vapor released by heating should be measured after heat treatment (e.g. the reaction $Fe^{2} + OH^{-} \rightarrow Fe^{3} + O^{2-} + \frac{1}{2}H_2$ would release H_2, while decomposition of carbonates would release CO_2). The magnetic properties should be recorded during heat treatment. In general we believe that we could reconstruct the mineralogy of the sample from sophisticated mineralogical studies plus knowledge of the total gas emitted and the change in the magnetic properties.

Now for details:

(1) anhydrous silicates. No significant changes. Diffusion is trivial below 500° C.

(2) hydroxylated silicates. Amphibole may undergo internal oxidation-reduction between Fe and OH but the basic structure would survive. Chlorite would probably undergo a similar change.

(3) zeolites. Would lose water when hot and regain it when cold. Would also sorb CO_2 and H_2 emitted by other minerals. The released water might enter other minerals causing hydration. Could be tricky. Some zeolites would retain their aluminosilicate framework (e.g. analcime) but others might collapse (e.g. stilbite).

(4) silicate glass. Should survive intact except perhaps for devitrification if basaltic. Rhyolitic glass would survive easily.

(5) sulfide. Bulk composition should survive, but diffusion between sulfides and phase changes (e.g. in pyrrhotite) might occur.

Dr. W. C. Phinney February 21, 1974

(6) carbonates. Calcite stable, magnesite fairly stable, $FeCO_3$ would probably decompose in vacuo. Stability depends on CO_2 content of atmosphere.

(7) hydroxides. Iron oxide-hydroxides would go to hematite in air. Might be more stable in vacuo. Could be interaction with gases released from other minerals.

(8) phosphates. Apatite stable. Basic iron phosphates might undergo complex reactions. Too difficult to spell out here.

(9) sulfates. Anhydrous ones might be stable, but hydrated ones would lose water.

(10) clay minerals. Very complex, but much would survive if heat treatment not too intense.

(11) sublimates. Many possibilities with many possible effects.

(12) CO_2-hydrate (clathrate structure). Would break down under any heat treatment above 10° C.

It is not easy to spell out all the possibilities, but you can see that there would be no difficulty in identifying high-temperature rock fragments such as basalt and rhyolite. Almost certainly we could identify hydroxides and carbonates either directly or from their remains. The worst problem would be sublimates and clathrate structures which would decompose totally even at room temperature. A key experiment on Mars would be to observe the sample with a stereomicroscope as the temperature was raised slowly up to 50° C.

Hope this is of some help.

Yours sincerely,

Joseph V. Smith

JVS/ib

copy: Dr. E. King
Dept. of Geology
University of Houston,
Houston, Texas

A. T. Anderson
J. R. Goldsmith
I. M. Steele

Memo TO: R. Brett

FROM: D. W. Strangway

RE: Some Measurements to be Made on Martian Samples (Physical Properties)

1) Was there an ancient Martian magnetic field?

A number of rock chips need to be measured for magnetic remanence and stability to alternating field and thermal demagnetization. From lunar experience it is difficult to make meaningful measurements on chips much smaller than one gram, and 5 gram chips are preferable. This measurement is of prime importance and is compromised strongly by heating. Even 100-150°C may have serious effects if very fine-grained particles (~100Å) of magnetic material are present, since these may grow in size (or change depending on the environment) and acquire stable magnetization of non-Martian origin. Goethite, a leading contender for Martian material, has a Néel point of about 120°C and it could be magnetized by heating above this temperature. Heating to 350°C (or less depending on grain size) will alter it to hematite and again confuse the magnetic result.

2) What are the magnetic minerals on Mars?

Leading contenders are goethite, lepidocrocite, hematite, magnetite, iron, iron-nickel, etc. Magnetic identification of these, together with a feeling for the grain size, can readily be done magnetically. It is probably safe to do some heating - as follows -

goethite → hematite
in air -- 350°C in 1/2 hour or so

iron-stable in vacuum to 800°C or more

fine-grained iron → iron oxides
in air as low as 100-150°C
magnetite → iron
∿500-600°C in vacuum

In other words, heating even over 100°C or 150°C will start to modify some of the magnetic minerals so they cannot be recognized magnetically in the returned samples. In view of the importance of the iron hydroxides in the Mars situation, it appears ~~to be~~ wise to heat the samples much over 100-150°C.

3) What are the dielectric properties of the Martian materials (at radar frequencies)

Since this has been one of the main tools telling us about the surface of Mars, we must study these properties in detail. The indications are that dielectric constant varies with altitude, tentatively implying that the mountains are rock and plains are soil. The amount of moisture present on Mars is not likely to have a major effect on the dielectric properties, but it is important to establish this, with careful experimental work on the Martian samples. This would simply bring back the samples under frozen conditions for the greatest relevance. Exposure to water and heating would certainly jeopardize the relevance of these measurements..

4) Do the surface materials have the optical properties detected from earth-based and orbital studies and can these observations be used to confidently map ~~the moon~~ Mars?

The spectral reflectance properties of Martian materials

also seems to be important. The controversial interpretations of its red color seem to make it particularly important to specifically tie down the properties of the surface and subsurface materials. If limonite is a serious contender, heating above 200 to 300°C would totally destroy this record. If glass has an important effect on optical properties (as it does in lunar materials), it should be kept below 500°C where major effects start to occur (or less if water vapor is present).

United States Department of the Interior
GEOLOGICAL SURVEY
Denver Federal Center
Denver, Colorado 80225

March 8, 1974

IN REPLY REFER TO:

Dr. Laurence E. Nyquist
Planetary and Earth Sciences Division
Code TN7
NASA/JSC
Houston, Texas 77058

Dear Harry:

This is a reply to your letter of Februray 15,1974 regarding a possible method of biological sterilization for Martian samples. I do not have much to add to Bruce Doe's "top of the head" suggestions, but I would like to restate it from a Pb researcher's eye.

1. Properties to be measured: I believe age determination studies of Martian samples are among the most important subject to be studied and I expect that the U-Th-Pb method will be included in the dating, because the $^{207}Pb/^{206}Pb$ ratios and related ages are not affected by very recent events (i.e. not dependent of the observed U/Pb ratios).

2. Effects of sterilization: We unfortunately do not have enough knowledge of sterilization procedures to know what is the best procedure for the U-Th-Pb system, and carefully designed experiments are needed. Our recent experiments show that about 58% of the total Pb was extracted from the "orange soil" 74220 when heated to 500°C for 12 hours in vacumm. Soils 12033, 12070 and 14259 released about 10%of their total Pb when heated 600°C in vacumm. Although we have not done a precise stepwise-heating experiment such as Ar workers have (e.g. Dr. Signer's experiments), I presume from the above stated results that some of the Pb migrates among minerals at 300°C heating. In any case, we must study carefully the sterilization effects on the U-Th-Pb system in minerals and rocks Which are most likely to occur on Mars.

Some attractive sterilization methods to me are (in order of preference):
i) Sterilization by rader waves.
ii) Incandenscent instant heating.
iii) The 150 C degree (or lower)heating for one month.

I would like to participate in the study group for testing effects of sterilization on the U-Th-Pb systems of minerals of Martian-like rocks, if NASA plans such experiments.

Sincerely,

M. Tatsumoto

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF PHYSICS

March 15, 1974

Dr. Robin Brett
Code TN7
NASA/Johnson Space Center
Houston, TX 77058

Dear Robin,

This will supplement the enclosed letter to S. Dwornik discussing Martian samples.

Speaking generally, practically all the measurements that have been made on lunar samples should be made on Martian samples, plus a few more based on the fact that Mars has an atmosphere. Concerning our three major experimental thrusts, I would rate the track and rare gas studies as high priority and thermoluminescence (TL) as a rather low priority. The TL might be interesting but it is difficult to prove that it is at this time.

Concerning the problem of alternative time-temperature treatments of the samples, it is clear and easily demonstrable that science is best served by keeping the temperature as low as possible, even at the expense of longer treatment times. For just about any process that would dissipate the information carried in the distribution of atoms in the samples (track annealing, gas diffusion, isotopic equilibration, TL annealing, etc.), the rate of the process would be proportional to $e^{-Q/kT}$. The activation energy Q would characteristically be of the order of 1 or 2 electron volts. For the proposed heating temperatures kT is a small fraction of a volt (room temperature is $\frac{1}{40}$ volt) and thus $Q/kT >> 1$. A relatively modest change in temperature gives a very large change in rate. For a specific example, if Q = 1 volt, T_1 = 350°C, and T_2 = 250°C, $Q/kT_1 \cong 19$ and $Q/kT_2 \cong 22$, so the process goes $e^3 \approx 20$ times faster at 350°C than at 250°C. Thus, a week at 250°C does less damage than a day at 350°C. Similarly, for the same Q, the process goes about 100 times slower at 150°C than at 250°C, and a month at 150°C is clearly preferable to a week at 250°C, and so on. The differences are more pronounced for higher Q, less for lower Q, e.g. for Q = 2 ev, the difference between 350°C and 250°C is more like a factor of five hundred. In general, any damage that has not already been done by the temperatures on the Martian surface would be minimized by using the lowest temperatures possible.

The real situation, of course, is more complicated and should be regarded as a composite of processes characterized by a range of activation energies. For the rare gases, for example, adsorbed gases (low Q) would probably be completely lost even at moderate temperatures like 150°C, while gases

embedded in the crystal structure (radioactive decay products, spallation products), with relatively high Q, would probably not be seriously affected by temperatures less than ∿500°C on any reasonable time scale. Similarly, we showed that tracks in lunar feldspars and pyroxenes are ∿50% annealed in 1 hour at 500°C, and we estimate that the same loss would occur in ∿60 days at 350°C. However, even low temperature annealing influences the tracks to some extent and modifies, for example, the track length distributions. By and large we would not expect large effects at 150°C (equivalent to the temperatures reached in lunar rocks) but would expect very noticeable effects at 350°C for a day. The latter treatment would degrade the information obtained but would not wipe it out. The TL degradation has the lowest Q and most of the scientific information obtainable from TL would probably be lost even by the 150°C treatment and almost surely be completely wiped out by 350°C.

In summary, the highest priority measurements (track and rare gases) would be only slightly affected by the 150°C treatment and could survive the 350°C treatment with some loss of scientific information. The TL would be severely affected at all heating temperatures. Whenever the choice is presented, heating for longer times at lower temperatures is clearly the way to go.

As a final thought, I wonder if the biologists have considered radiation sterilization? Prodigious doses of γ-rays in the 1 to 5 MeV range would of course destroy any scientific information that derives from the study of trapped electrons (e.g. thermoluminescence) but would leave most other properties unaffected. This is probably something that should be looked into very seriously.

I have not discussed the proposal to "heat the samples to incandescence." The phrase has a certain ring to it but is imprecise. If you mean to vaporize the sample and break it down into its constituent ions, I guarantee that this will destroy any living organism. Are you kidding?

Best regards,

Bob Walker

Robert M. Walker
Professor of Physics

RMW:hk
Enclosure

MAX-PLANCK-INSTITUT FÜR CHEMIE
(OTTO-HAHN-INSTITUT)

FERNSPRECHER 25044
MAINZER VOLKSBANK 28567
Abteilung Kosmochemie
Direktor: Professor Dr. H. Wänke

6500 MAINZ, DEN
SAARSTRASSE 23
SCHLIESSFACH 3060

Dr. Larry Nyquist
NASA
Lyndon B. Johnson Space Center
Houston, Texas 77058
U.S.A.

March 7, 1974

Code: TN 7

Dear Dr. Nyquist:

In the exploration of mars as of any other planet for a geochemical point of view element correlations will be of major importance. From the research on lunar samples the significance of element correlations became evident. All lunar samples showed identical values for many element ratios like Fe/Mn, K/La, K/Ba, W/La and to a somewhat smaller degree Fe/Sc and several others. One should therefore take great care to avoid any possible contamination for these elements. The W/La-ratio is of special interest as W is only partially lithophile and actually the major portion of W on the moon must reside in a metal core or layer. Hence, we have an ideal case to estimate the metal/silicate ratio of planets. (The samples of Luna 16 and Luna 20 for example showed high contamination in W).

As for the moon, for the parent planet of the eucrites and to some extend for the earth, the correlated elements will provide a geochemical framework for the estimation of the bulk chemical composition of mars.

The sterilization procedures should ,of course, avoid all possible contaminations. Dry heat sterilization in sealed containers should be preferred. Sterilization with addition of water vapour is the worsest what could be done. As far as time-temperature relation for the sterilization is concerned, case a) - long time-low temperature - will do least harm to the problems in mind which in general rely on trace element concentrations and distributions.

This is in short what I can say at the moment in this respect.

Yours sincerely,

H. Wänke

THE UNIVERSITY OF UTAH
COLLEGE OF MINES AND MINERAL INDUSTRIES
SALT LAKE CITY 84112

DEPARTMENT OF GEOLOGY
AND GEOPHYSICS

717 MINERAL SCIENCE BUILDING

March 4, 1974

Dr. Robin Brett
National Aeronautics and
Space Administration
Mail Code: TN7
Lyndon B. Johnson Space Center
Houston, Texas 77058

Dear Robin:

Last week we held a meeting of W. E. Glenn, W. P. Nash, W. J. Peeples, R. W. Shorthill, W. R. Sill, R. C. Wilson, and myself for the purpose of preparing a report to you on Martian sample sterilization. The attachment is a summary of the properties which might be measured, their priority in terms of understanding Mars, and our guess of degradation by elevated temperature environments.

We would recommend that the most acceptable treatment, of those you list, is "Dry heat sterilized in a sealed container at 150° for 1 month".

The needed research is simple: develop simulated Martian materials, subject them to one or more of the proposed environments, and evaluate the degree of degradation of knowledge -- for each property -- by application of the environment.

Our preference would be to avoid any sterilization by returning the samples to a space shuttle station for measurements. Alternatively, make the key measurements in Martian orbit and then sterilize the sample.

I hope that this brief report will assist you.

Kindest regards,

S. H. Ward
Chairman

SHW:mm

PROPERTIES TO BE MEASURED ON A RETURNED MARTIAN SAMPLE

			Priority
I.		Petrology - directed toward knowledge of interior of Mars	
	Δ	1. primary mineralogy	2
		2. petrographic texture	3
		3. petrofabrics	3
	*	4. geochronology (K-Ar Sr-Rb)	1
		5. glass component	4
II.		Surficial material - directed toward study of surface processes	
		1. Weathering products	
	Δ 0	a) oxides and hydroxides - mineralogy and chemistry	3
	** Δ 0	b) clays - mineralogy and ion exchange capacity	2
	* Δ 0	c) other hydrates such as opal - mineralogy and chemistry	3
	* Δ 0	d) contained liquids and gases	3
		2. Soil mechanical properties	5
		3. Sediment petrography	
		a) grain size	4
	** Δ 0	b) clay composition	2
	** Δ 0	c) mineralogy	4
III.		Other Properties	
		A. Geophysical	
		a) density	5
	* Δ 0	b) electrical properties	4
	Δ 0	c) thermal conductivity	2
	* Δ	d) elastic parameters	2

			Priority
**		e) magnetic properties	2
	Δ 0	f) optical spectral reflectance	3
		B. Geochemical	
		a) radioactive spectrum	2
*		b) isotopes	2
	Δ 0	c) gas content	2

Legend:

* Degraded by sterilization at 200^{0}C and above.

** Possibly degraded by sterilization at 150^{0}C and above.

0 Degraded by exposure to interplanetary vacuum.

Δ Degraded by adding water.

We assume slow heating and cooling.

From Wasserburg 231

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF GEOLOGICAL AND PLANETARY SCIENCES

TELEPHONE (213) 795-6811

30 January 1974

Dr. Stephen E. Dwornik, Chief
Planetology Program
Planetary Programs, Office of
Space Science
NASA Code SL
Washington, D. C. 20546

ORIGINAL PAGE IS
OF POOR QUALITY

Dear Dr. Dwornik:

This letter is in response to your letter of 20 December regarding a study by the Planetary Programs Office to determine the feasibility of a Mars Surface Sample Return mission.

Let me first indicate that this laboratory is very interested in participating in isotopic experiments to determine the extent of sample degradation which may be caused by various sterilization procedures. There are two critical studies which should be made in this area. One is the extent of rare gas loss by sample heating, and the other is X-irradiation. These studies should include the range of heating and/or X-irradiation in the realm of those considered for sterilization procedures. These analyses should also be done on a variety of materials including terrestrial, meteoritic, lunar and also, possibly, synthetic materials which might resemble a martian soil (both hydrous and anhydrous). In addition, studies of Rb, Sr and Pb should be carried out on the same samples, in order to assess the effects on these elements in the constituent mineral phases. We would be willing to undertake such studies on a contract or grant basis, and would be willing to utilize samples with other workers who would undoubtedly be studying mineral degradation as a result of sterilization.

There are several other laboratories throughout the world with people of such competance which could contribute effectively to the program as proposed in your letter. These include Dr. Peter Signer (ETH-Mineralogical Institute, Zurich, Switzerland), Johannes Geiss (Universitat Berne, Physikalisches Institut, Berne, Switzerland), Edward Anders (The Enrico Fermi Institute for Nuclear Studies, The University of Chicago), Kurt Marti (Department of Chemistry, University of California, La Jolla, California), Roman Schmitt (Department of Chemistry, Radiation Center, Oregon State University), Larry Haskin (Planetary and Earth Sciences Division, Johnson Space Center, Houston), Ray Siever (Department of Geological Sciences, Harvard), Cliff Frondel (Geological Sciences Department, Harvard), Robert Walker (Department of Physics, Washington University, St. Louis, Missouri), Robert Fleischer (Research Laboratory, General Electric Company, Schenectady, New York), John Philpotts (Planetology Branch, Goddard Space Flight Center), John Wasson (Institute of Geophysics, University of California, Los Angeles), and Gordon Goles (University of Oregon, Center for Volcanology, Department of Geology).

CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA, CALIFORNIA 91109

Dr. Stephen E. Dwornik, Chief
Planetology Program

30 January 1974

Page two

I am certain that there are many others who could contribute significantly to the solutions of the problems which you have posed in your letter. I would certainly hope that capable people, knowledgeable in the alteration of fine grain terrestrial sediments would be among the participating members.

I have just spoken with Professor Hans Eugster of the Johns Hopkins University who is extremely knowledgeable about processes and problems regarding [illegible] sedimentation. He indicated that he would be quite willing to participate in a Mars study, as indicated. He is uniquely qualified to give new and imaginative insights.

In this laboratory, the prime person who would wish to carry forward the researches would be John C. Huneke, Senior Research Fellow. He has indicated to me that he would be willing to participate in this problem and to aid in some of the planning stages of problem definition and analysis.

Very truly yours,

G. J. Wasserburg
Professor of Geology
and Geophysics

GJW:kr

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF GEOLOGICAL
AND PLANETARY SCIENCES

TELEPHONE (213) 795-6811

15 November 1973

Dr. Michael B. Mc Elroy, Chairman PSC
Pierce Hall G3A
Harvard University
Cambridge, Massachusetts 02138

and

Members of PSC

Gentlemen:

This note is to report on the Mars Sample Return Symposium at Ames on 24 and 25 October. The "conference" lasted two days and was rather loosely organized, so that no proper motion or action was taken by the participants. nonetheless, it is my impression that a strong consensus existed on the basic issues. These basic items are as follows:

1. There was a strong desire to pursue a Mars sample return mission with sterilization. No "in principle" opposition to a sterilized sample return was evident from the participants, including both Josh Lederberg and Carl Sagan.

2. The definition of sterilization and the mechanism by which sterilization could be accomplished (thermal, time, chemical, irradiation . . .) is uncertain and requires adequate definition.

3. The effects of possible sterilization procedures on the science ontent of a returned sample (both Inorganic, physical, "biochemical" and morphological) are unknown and must be assessed.

4. The Agency must aid ICBC in seeking and defining legitimate, operable sterilization and quaranteen requirements for the "importing" of extraterrestrial materials. The lunar quaranteen fiasco, which subjected lunar samples to enormous risks, whould not be repeated.

CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA CALIFORNIA 91109

Dr. Michael B. McElroy
Members of PSC

15 November 1973

The above conference conclusions also implied action items which required prompt response from the Agency and the general science community if the matter of sample return is to be pursued.

1. A range of possible operable definitions of sterilization must be stated by a small group of knowledgeable scientists. This group would have to consist predominantly of non NASA personnel.

2. Experiments must be undertaken by scientists specializing in "biochemical", chemical, physical and organic life form (morphology) fields for the purpose of ascertaining the extent of sample degradation by various sterilization procedures (see 1 above) on model Mars materials. Again, this should not be carried out solely by NASA personnel.

3. The ICBC requirements for sterilized sample return and quaranteen must be defined so that only a small part of a Mars sample is used for ICBC protocol. The ICBC must re-evaluate the lunar experience and adequately define the circumstances under which the quaranteen restriction may be satisfied.

Very truly yours,

G. J. Wasserburg
Professor of Geology
and Geophysics

GJW:kr

x. c. J. Naugle
D. Young

United States Department of the Interior

GEOLOGICAL SURVEY
WASHINGTON, D.C. 20242

March 6, 1974

Dr. W. C. Phinney
Chief, Geology Branch
Johnson Space Center Code TN7
Houston, Texas 77058

Dear Bill:

We had our discussion on the Martian sterilization procedure. Ed Roedder has a separate report to Elburt King which I shall not reiterate here.

The general feeling is that any heating might be deleterious to carbonates and clay minerals, both to their composition and morphology. We feel that rate studies on carbonates and clay minerals should be done in conjunction with the organic decomposition rate studies to obtain optimum heating-time integrals.

George Faust felt that you would run a good chance of forming siderite from limonite + CO rich atmosphere if you heated it up. There are a wide variety of hydrous metastable carbonates that could form from exposure to a humid CO_2 rich atmosphere. George also felt that fluorine could form enamel-like compounds if very fine grained fluorides are present.

Moto Sato felt that most of the mineral assemblages on the Martian surface would be metastable and hence very susceptible to any maltreatment like heating.

Mac Ross and I are very concerned about auto-oxidation effects caused by heating in vacuo or inert gases and preferentially driving off hydrogen from ferrous iron-hydroxyl compounds (clays, micas, amphiboles, hydrous phosphates, carbonates and sulfates) leaving the ferric compound as the residua. This would negate H/D isotopes studies, H_2O bulk chemistry, Fe^{2+}/Fe^{3+} ratios, densities, and any spectral work which involved charge transfer processes (visible, ESR, Mossbauer, etc.).

Rosalind Helz came up with the best suggestion of all. Collect two samples. Sterilize one and check it for beasties. If it is clean, then open up the pristine sample for sample analysis.

I will be glad to amplify any of these, if needed, but I feel the kinetics program is the best positive suggestion, along with Ros' idea.

See you next week, especially the 19th.

Best regards,

David R. Wones

APPENDIX III

Progress Report

Preliminary Study of Dry Heat Sterilization Effects on Inorganic Science for a Returned Mars Surface Sample

Department of Geology
University of Houston
Houston, Texas 77004

March 27, 1974

Preliminary Study of Dry Heat Sterilization Effects on Inorganic Science for a Returned Mars Surface Sample

Summary

The brief study has involved eight laboratories and a number of different analytical techniques to characterize five model samples which are possibly analagous to some fraction of the Martian surface. The object of the study is to attempt to estimate, based on the analyses and data in the literature, the seriousness of sample inorganic degradation resulting from dry heat sterilization of the very short time available for this study, all results should be considered as preliminary. Also, it is obvious that the general conclusions reached are applicable only to the materials studied and will not apply to other samples.

A number of changes in chemistry and mineral phases present were noted in most of the samples as a result of heating to as much as 275°C. The changes mostly involve loss of volatile components. U. S. Geological Survey rock standard diabase W-1 was the least affected by heating.

The sterilized sample still retains an immense amount of inorganic science information and is of extreme scientific interest. If the temperature profile of the sterilization is well known, much of the information lost can be reconstructed. Also, if the identities of the gaseous species that are lost can be determined, the chemical and mineralogical sample changes can be interpreted rather completely.

If there are trade offs to be made on sterilization conditions, it appears that the lowest possible temperature is desirable from an inorganic point of view, even though the time required for sterilization may be longer.

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Further work on other samples and the same samples is in progress, but it does not appear that an extensive program of experimental work of this type is justified until there is much better information on the chemistry and/or mineralogy of the Martian surface and the actual conditions of sterilization that will be required.

CONTENTS

Introduction (E. A. King)

Preparation and Handling of Reference Preliminary Mars Sterilization Study Samples (J. C. Butler and E. A. King)

Effects of Sample Sterilization on Mineral Phases by x-ray Powder Diffraction (Butler, J. C.)

Effects of Sample Sterilization on Mineral Phases by X-ray Powder Diffraction (J. V. Smith)

Effects of Sample Sterilization on Data Obtainable from Fluid Inclusions (E. Roedder)

Major and Miner Element Chemical Analyses (P. Johnson)

Uranium, Lead and Thorium Analyses (M. Tatsumoto)

Weight Loss Studies and Analyses for Sodium, Rubidium and Lithium (J. Philpotts, D. Nava, S. Winzer and R. Lum)

Gas Release Curves and Weight Loss Studes (E. Gibson and G. Moore)

Oxygen Isotope Analyses (R. N. Clayton)

Documentation of Selected Samples (I. C. Jones)

Preliminary Study of Dry Heat Sterilization Effects on Inorganic Science for a Returned Mars Surface Sample

Introduction

E. A. King

A possible planetary mission option now under consideration in NASA Headquarters is the return by an unmanned spacecraft of a small surface sample from Mars. It appears that various government regulatory agencies will require that the sample be sterilized prior to possible entry into the terrestrial biosphere in the event that the mission is approved. Dry heat is the means of sample sterilization presently under consideration. However, heating of the sample will degrade the inorganic information content.

In order to get an estimate of the magnitude of information loss for the inorganic sciences, particularly mineralogy, petrology and geochemistry, the Planetology Programs Office of NASA Headquarters requested that we undertake a short term analytical study and literature survey in cooperation with a number of established laboratories. The program was neither designed to be comprehensive nor thorough, but only to give "order of magnitude" indications of some of the problems that might be encountered and some of the information content that might be preserved.

Individuals and Institutions participating in this preliminary study include the following:

J. V. Smith, Univ. Chicago
I. M. Steele, Univ. Chicago
Edwin Roedder, U. S. Geological Survey
Pratt Johnson, NASA JSC and Univ. Houston
M. Tatsumoto, U. S. Geological Survey
J. A. Philpotts, NASA GSFC
D. F. Nava, NASA GSFC
S. R. Winzer, NASA GSFC
R. Lum, NASA GSFC
E. Gibson, NASA JSC
G. Moore, NASA, JSC

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R. N. Clayton, Univ. Chicago
J. C. Butler, Univ. Houston
I. C. Jones, Univ. Houston
E. A. King, Univ. Houston

During the course of the work, NASA JSC was given the responsibility for proceeding with a broader based study relying on the experience of a large number of individuals and the previous literature. Thus, these experimental data are here incorporated into this larger effort.

Six reference samples were chosen for this preliminary study, four for inorganic reasons and two for the convenience of microbiologists whose work will be reported elsewhere. The six samples are W-1 (USGS rock standard diabase), Murchison meteorite (a well analyzed carbonaceous chondrite Type III fall - selected partially for its organic content), "Limonite" (Ward's Nat. Sci. Estab.), Montmorillonite (Ward's Nat. Sci. Estab.), Hesperia soil (microbiological standard) and Waukena soil (microbiological standard). These samples were heated in aliquots to 150°C under low atmospheric pressure (100 ml) and to 275°C under an He atmosphere. Appropriate aliquots of the heated and unheated samples were distributed to the participants for analysis. Literature data on these and similar samples are included.

The extremely short time schedule that was required for the study di not allow for a more comprehensive suite of samples nor for their more elaborate preparation. Similarly, there was considerable pressure on analysis to produce results within only a few weeks; thus, all of the analytical data included herein should be considered as preliminary. However, care was taken to homogenize all samples and to treat aliquots of the same sample identically. The goal was not to create new rock and mineral standards, but to compare the results from heated and unheated sample

splits to see the effects of dry heat, if any.

Several hundred grams of unheated reference samples are still intact in our laboratory and our facilities for heating samples under vacuum or under gaseous atmospheres are now much improved. We will be glad to make additional heating runs, runs at higher temperatures, or runs for special purposes and furnish sample splits to others as requested.

Work in our own laboratory is continuing at a more modest pace on additional samples and also different sterilization conditions for these same samples and their mixtures are being investigated. These will be reported to NASA together with the data herein sometime this fall.

PREPARATION AND HANDLING OF REFERENCE PRELIMINARY MARS STERILIZATION STUDY SAMPLES

W - 1 (U. S. Geological Survey Standard Diabase, Jar # 36) -

Unheated splits - Our sample of W-1 was rolled, quartered several times on glassine powder paper, using stainless steel spatulas. Individual aliquots were transferred to another powder paper, weighed and poured directly into the sample vials, which are polystyrene bases with polyethylene caps.

Heated to 150°C for 72 hours under vacuum (100 ml) - Aliquots of approximately ten grams were poured from glassine powder paper into wide aluminum boats, handmade with stainless steel tools from a fresh roll of aluminum foil. The samples were thinly spread out in the bottom of the boats with a stainless steel spatula and placed in a vacuum furnace. The vacuum pump (oil diffusion pump) was turned on and when the pressure reached 100 ml of mercury, the heating elements were turned on. The furnace reached 150°C in approximately one hour and was held at that temperature for 72 hours. The heating elements were then turned off and the furnace cooled to room temperature over a period of approximately four hours. Air was then slowly bled into the furnace and when the pressure reached that of ambient atmosphere, the samples were removed. They were then poured onto powder paper, rolled and quartered into approximately 1 gram aliquots with a stainless steel spatula, weighed and poured directly into the vials.

Heated to 275°C for 24 hours in helium atmosphere - Procedure was the same as for the 150°C samples except that the samples were placed in a furnace with a helium gas inlet system, the surface volume was flooded with helium and the furnace was heated to 275°C over a period of approximately two hours and held at that temperature for 24 hours. The heating elements were then turned off and the furnace reached room temperature over a period of approximately 6 hours. During the heating, and cooling of the furnace the sample chamber was under a continuous flow of helium. The samples were then removed from the furnace rolled and quartered on glassine powder paper into approximately one gram aliquots using stainless steel spatulas, weighed, and poured directly from the powder paper into the standard vials.

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Murchison Meteorite -

Unheated splits - A small fusion crusted individual stone with a visually clean surface was wrapped in several layers of fresh aluminum foil and broken into a number of small fragments with a hammer. Approximately 150 grams of this crudely pulverized material was then placed directly from the foil into the freshly cleaned chamber of a Spex Industries "Shatterbox" and reduced to fine aggregate in approximately 30 seconds of aggitation. The chamber of the shatterbox was cleaned by pulverizing quartz for an extended period and then being blown out with dry laboratory air. Careful inspection of the chamber prior to introduction of the meteorite material did not reveal the presence of any residual or foreign particles. From the shatterbox chamber the finely pulverized sample was poured into a clean alumina mortar and further ground by hand with an alumina pestle. The sample was then sized by sieving in U. S. Standard Sieves to less than 62.5 micrometers. Subsequent handling was the same as for W-1 above.

Heated to 150°C for 72 hours under vacuum (100 ml) - Handling and procedure same as for unheated splits (see above) and for similarly heated samples of W-1 (see above).

Heated to 275°C for 24 hours in helium atmosphere - Handling and procedure same as for unheated splits (see above) and for similarly heated aliquots of W - 1 (see above).

"Limonite" (furnished by Ward's Natural Science Establishment, variety Yellow Ocher, from Cartersville, Georgia).

Unheated splits - The limonite came as a fine powder. It was not pulverized in any way, but was only ground by hand with an alumina mortar and pestle. Subsequent handling was identical to unheated samples of W-1 (see above).

Heated to 150°C for 72 hours under vacuum (100 ml) - Handling and procedure same as for unheated splits (see above) and for similarly heated samples of W-1 (see above).

Heated to 275°C for 24 hours in helium atmosphere - Handling as for unheated splits (see above) and for similarly heated aliquots of W-1 (see above).

Montmorillonite (furnished by Ward's Natural Science Establishment, Montmorillonite # 24, 48 W 1240, Otay, California) -

All montmorillonite samples were handled identically to similar heated and unheated aliquots of the Murchison meteorite (see above).

Hesperia Soil (microbiological standard, furnished by Dr. Keith Kvenvolden, NASA Ames Research Center) -

The bulk sample was sieved in U. S. Standard Sieves to less than 44 micrometers. All fractions of the sample were then handled and processed identically to W - 1 (see above).

Preliminary Mars Sample Study - effects of sample sterilization on data obtainable from x-ray powder diffraction

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X-Ray Powder Diffraction Analysis

All of the X-ray powder diffraction analyses described in this section were accomplished with a Phillips Norelco diffractometer using Ni-filtered CuK_a radiation. Unless otherwise noted, samples were prepared by sedimentation from an acetone slurry onto glass slides and by packing the powder into an aluminum sample holder. Acetone does not appear to have had any effect on the d-spacings measured.

Waukena Soil

The Waukena soil samples have not been distributed for extensive mineralogical and chemical analysis. This sample, however, submitted with the Hesperia soil sample for analysis to the Ames Research Center.

A total of 597.05 grams of Waukena soil was received from the Ames Research Center. The sample was homogenized and quartered and an analysis of the grain size frequency distribution was undertaken using a randomly selected quarter of the parent sample. A plot of the cumulative frequency distribution using a probability ordinate is given in Figure 1 along with measured values of the graphic mean grain size (M_z), graphic median (M_d), graphic skewness (S_{kG}) and graphic standard deviation (σ_G).

Preliminary x-ray powder diffraction analysis indicates that the majority of the Waukena sample is composed of plagioclase and quartz. There are minor amounts of an illite-like component (a 10Å clay mineral) and a montmorillonite type compound.

Hesperia Soil

Hesperia soil samples have been distributed to the Ames Research

Center for organic analysis and to the other investigators for mineralogical and chemical analyses.

A total of 560.64 grams of Hesperia soil was received from Ames; the sample was homogenized and quartered. A plot of the cumulative frequency distribution for a randomly selected quarter of the Hesperia parent sample is given in Figure 2 along with the measured values of the summary statistics.

Preliminary x-ray powder diffraction analysis indicates that the Hesperia sample consists primarily of quartz and feldspar (both plagioclase and an alkali feldspar). Minor phases include an illite-like component with a 10Å basal spacing, an amphibole (?), a mixed layer clay mineral, gypsum (?) and a 14Å clay mineral (?). Tracings of powder diffraction patterns from 32° to 2° 2θ are given in Figure 3 for the natural sample, the sample heated in vacuum and the sample heated in helium. Predominate changes are those involving the clay mineral components. The illite-like component exhibits a 10Å (001) maximum that sharpens after both heat treatments and the mixed layer component essentially disappears following the treatment at 275°C. In addition, the pattern for the material heated at 275°C exhibits several "humps" of diffraction intensity (centered around 20°, 17° and 13° 2θ) that appear to reflect the development of material that is amorphous to x-rays. The questional gypsum line is eliminated following both heat treatments.

It would appear advisable to attempt to separate the Hesperia sample into its components (using heavy liquids) for future analyses.

Otay Montmorillonite

One pound of the Otay (California) montmorillonite was obtained from

Wards Natural Science Establishment, Inc. This sample was collected in 1955 by Dr. R. J. Holmes of the Department of Geology at Columbia University from the same area as was the A.P.I. Otay Montmorillonite clay mineral standard that was collected in 1947 by Dr. L. J. Kulp.

The material received from Wards was quartered and ground as described previously. The powder was sieved with a 1.0Ø increment. Material less than 4 Ø was distributed to the Ames Research Center for organic analysis and to other investigators for mineralogical and chemical analyses.

Preliminary x-ray powder diffraction samples were prepared by mixing the fine powder with deionized water and pouring the slurry onto glass slides. The basal spacing (001) is 15.2Å which is indicative of a Ca-rich montmorillonite. The basal spacing expands to 17.7Å following heating for 2 hours in ethylene glycol vapor at 75°C and collapses to 9.9Å following heating at 325°C in air for 24 hours. In addition to the montmorillonite phase, minor amounts of quartz and illite are present. A tracing of the diffraction pattern from the natural, glycolated sample is given in Figure 4. Tracings of diffraction patterns of the natural, glycolated and collapsed samples (prepared from a water slurry) are given in Figure 5.

Samples that had been heated for 72 hours in vacuum and for 24 hours at 275°C in helium were scanned from 16° to 2° 2θ within 15 minutes after removal from the furnace. Tracings of diffraction patterns from 12° to 2° 2θ for the natural sample, the sample heated at 150°C for 72 hours in vacuum and the sample heated at 275°C for 24 hours are given in Figure 6. Diffractograms of the heat treated samples were prepared approximately 24 hours after turning off the furnace and allowing the samples to cool to room temperature under the experimental conditions (that is, in vacuum or with

helium flowing over the samples). Following both heat treatments the basal spacing (001) collapsed to 14.5Å. The basal spacing of material heated at 275°C is more asymmetrical than is the basal spacing of material heated at 150°C in vacuum. As indicated in Figure 4 , heat treatment at 325°C resulted in collapse to 10Å. Differences between material heated at 275° and 325°C may be the result of temperature differences and/or differences in grain size. The material heated at 275 °C in helium was the less than 4Ø fraction whereas material heated at 325°C in air was sedimentated onto a glass slide from a water based slurry and it is likely that the finest particles were at the top of the slide. An additional sample was prepared by sedimentation from a water based slurry and heated at 275°C in helium. Diffraction patterns from this material were prepared within 5 minutes after rapidly cooling to room temperature. Additional scans were made at 20 minute intervals .Tracings of diffraction patterns made after 5 minutes, 20 minutes, 40 minutes and 60 minutes are given in Figure 7 . Within 5 minutes after removal from the furnace the basal spacing is collapsed to almost 10Å. Increasing time at room temperature and at a relatively humidity of approximately 60% results in a decrease in the intensity of the 10Å maximum and development of a broad "hump" in the vicinity of 6° 2θ (14.5Å).

It is apparent that the heat treatment used in this study did not result in the permanent collapse of the sample. The sample illustrated in Figure 7 was heated for 2 hours at 75°C in ethylene glycol vapor and the sample expanded to approximately 17.5Å. That is, heat treatment at 275°C resulted in a collapse of the original structure to approximately 14.5Å but the material retained the capability for expansion.

Behavior of clay minerals during sterilization procedures is probably going to be very complicated and it suggested that additional clay mineral components be included in preliminary studies.

Limonite

Approximately 550 grams of limonite (variety yellow ocher) was purchased from Wards Natural Science Establishment, Inc. This particular material was collected near Cartersville, Georgia. Samples of the finely powdered material were distributed to the Ames Research Center for organic analysis and to the other investigators for chemical and mineralogical analyses.

Tracings of the diffraction powder patterns of the natural sample, the sample heated in vacuum at 150°C for 72 hours and the sample heated at 275°C for 24 hours are given in Figure 8. The natural sample contains goethite and quartz as crystalline phases; in addition, there is an unknown amount of material that is amorphous to x-rays. This amorphous material is most likely a mixture of hydrated oxides or iron. Heating at 150°C in a vacuum for 72 hours results in a decrease in the amount of goethite and there is a small amount of hematite produced. Heating at 275°C for 24 hours results in the destruction of the goethite and formation of hematite. Detailed experiments are planned in which the rate of change from goethite to hematite is studied in detail.

W 1

Approximately 50 grams of W 1 were available for this study. Preparation of the W 1 samples has been previously reviewed. The sample used in this study was from vial # 36.

Tracings of powder diffraction patterns of the natural sample, the sample heated in vacuum for 72 hours at 150°C and the sample heated for for 24 hours at 275°C are given in Figure 9. The natural sample consists of subequal amounts of augite and plagioclase with minor amounts of quartz and accessory minerals. The framework silicates exhibit no detectable changes. The illite line (001) appears to decrease in intensity following heat treatment and it is possible that there are some amorphous clay-like phases present.

Murchison Meteorite

Approximately 250 grams of the Murchison meteorite was obtained from Dr. E. Olson. The sample preparation has been previously described.

Tracings of powder diffraction patterns of the natural sample, the sample heated at 150°C for 72 hours in vacuum and the sample heated at 275°C for 24 hours in helium are given in Figure 10.

The patterns are of relatively low quality. However, the most intense maxima of diopside and olivine can be identified. In addition, the sample contains what appears to be a sheet silicate with a 14Å basal (001) spacing. The 14Å spacing is very poorly developed whereas the 7Å (002) and 3.5Å (004) spacings are better developed. This component appears to be present following treatment at 150°C in vacuum although the 14Å maximum is not present. Following treatment at 275°C for 24 hours in helium, both the 14Å and 43.5Å maxima have disappeared and the 7Å material is reduced in intensity. Most likely this material is an iron-rich sheet silicate; that is, an iron-rich chlorite.

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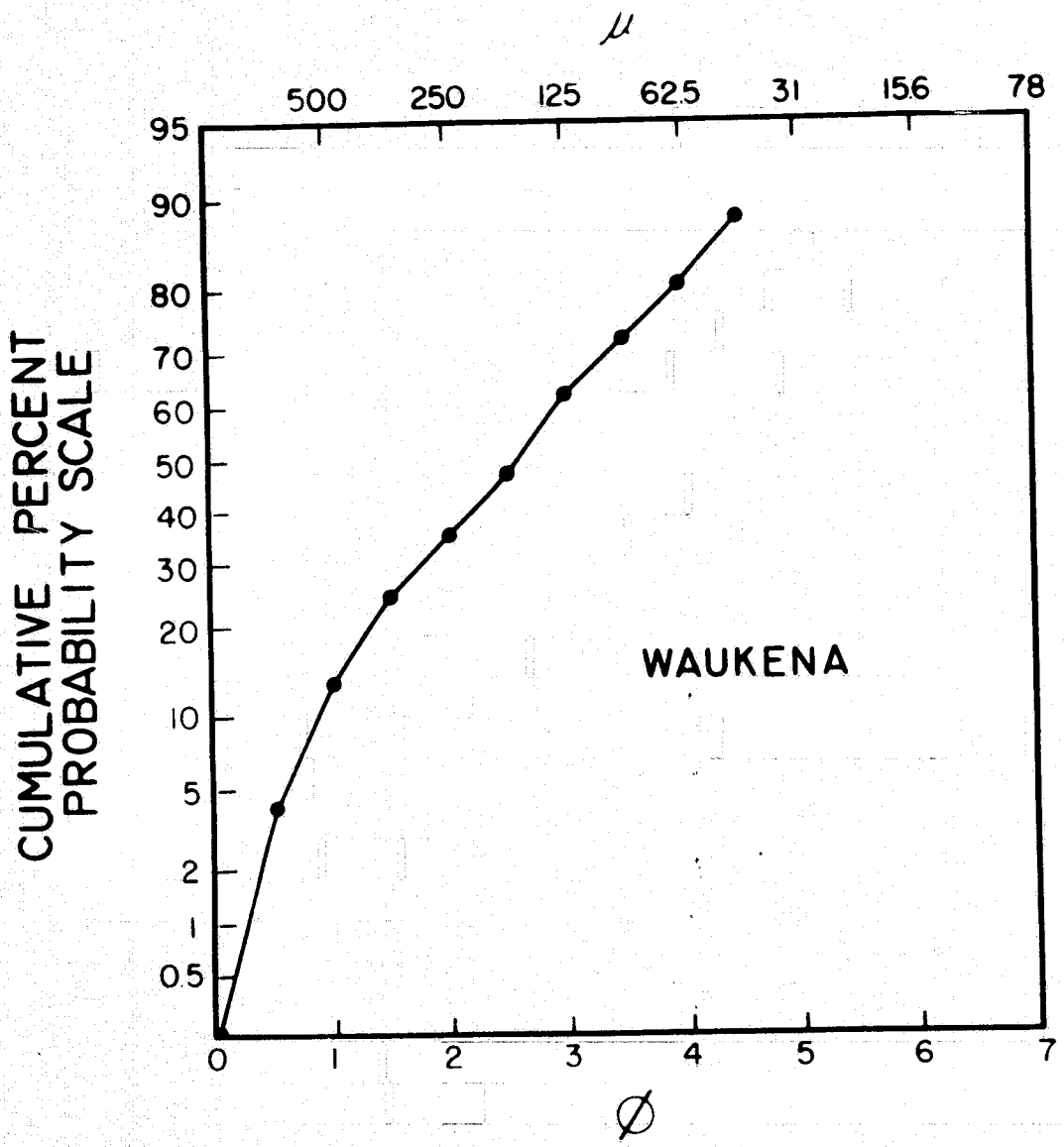


Figure 1. Cumulative frequency distribution of the Waukena soil sample. Graphic median equals 2.10Ø, graphic mean grain size equals 2.2Ø, graphic standard deviation equals 1.45Ø and graphic skewness equals +0.10.

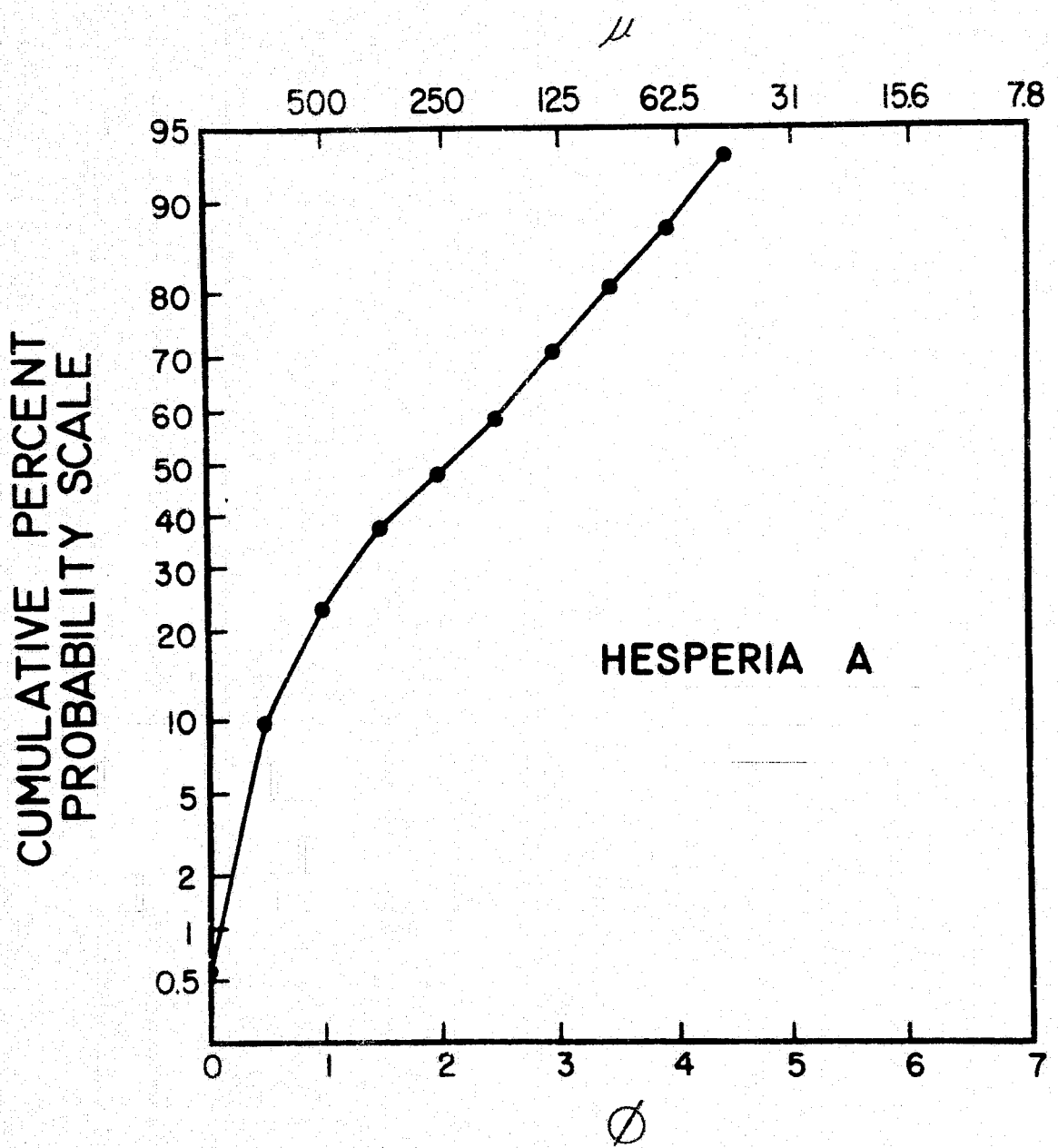


Figure 2. Cumulative frequency distribution of the Hesperia soil sample (subsample A). Graphic median equals 2.58Ø, graphic mean grain size equals 2.63Ø, graphic standard deviation equals 1.55Ø and graphic skewness equals +0.29.

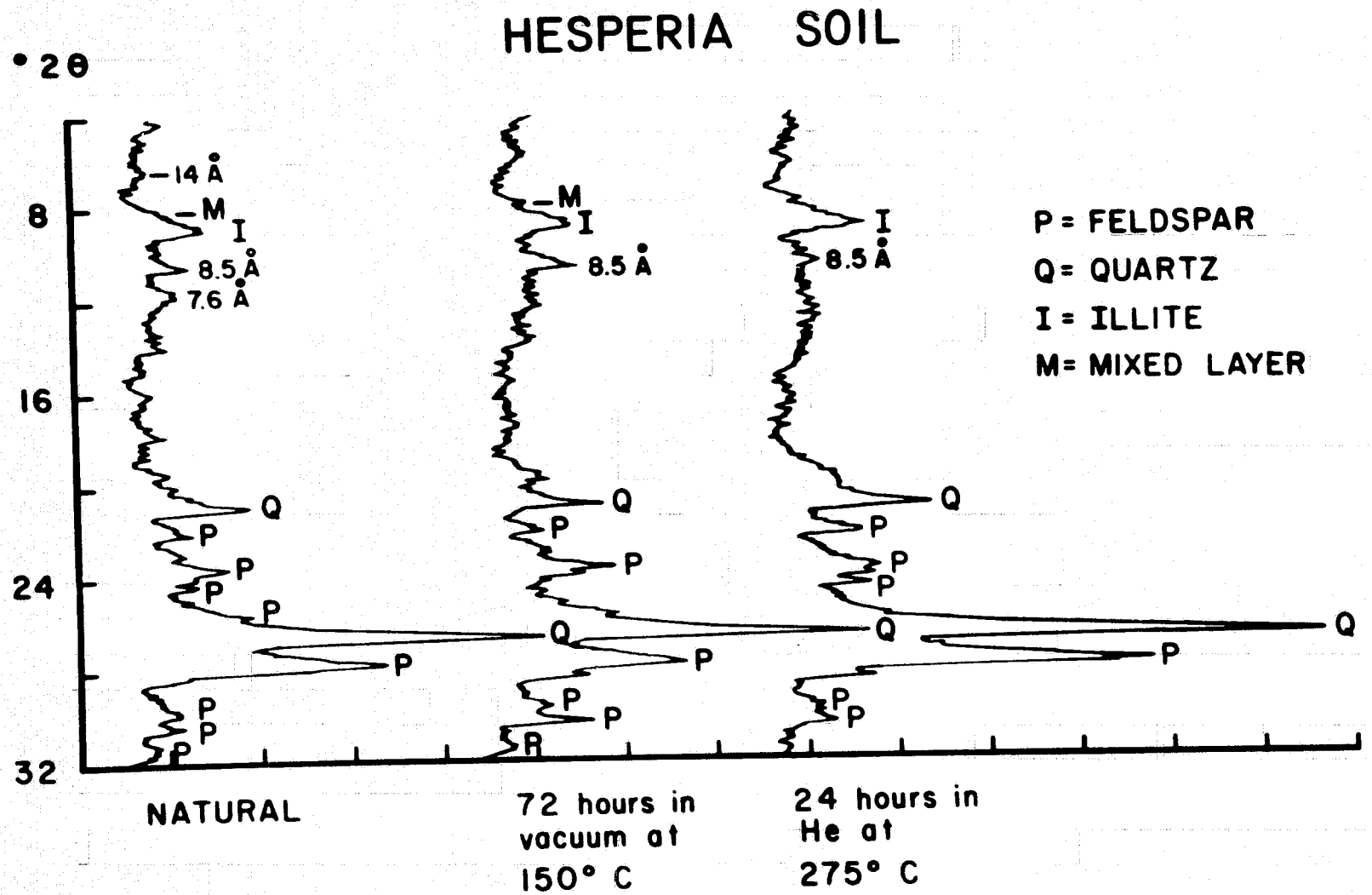


Figure 3. Tracings of x-ray powder diffraction patterns of natural and heat treated samples of Hesperia soil.

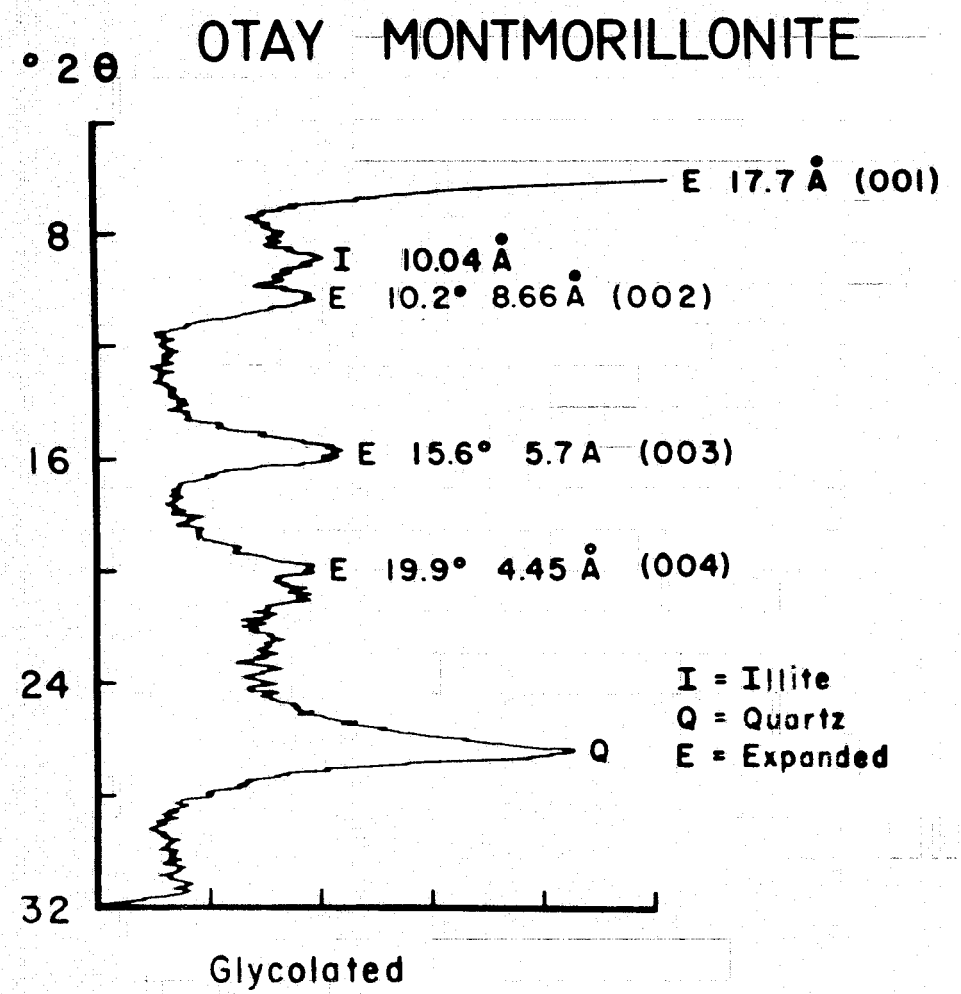


Figure 4. Tracing of x-ray powder diffraction pattern of a glycolated sample of the Otay Montmorillonite

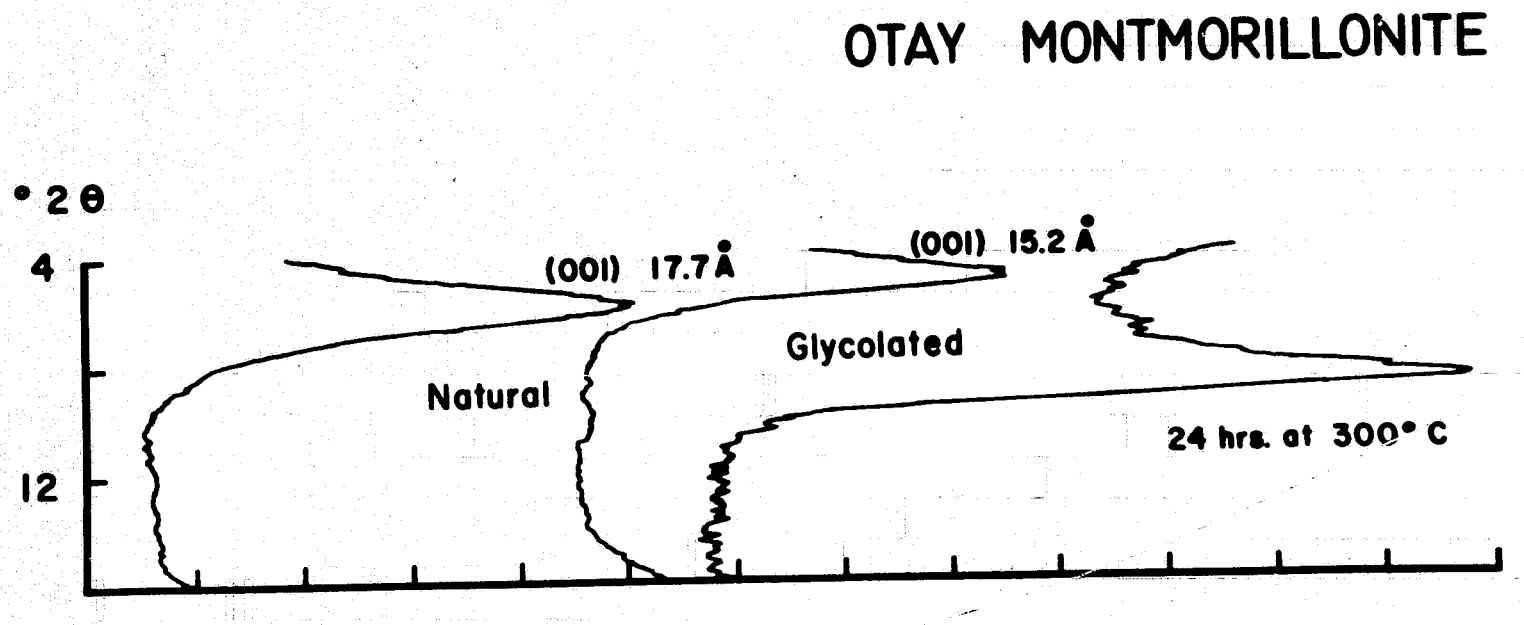


Figure 5. Tracings of x-ray powder diffraction patterns of natural, glycolated and collapsed samples of the Otay Montmorillonite.

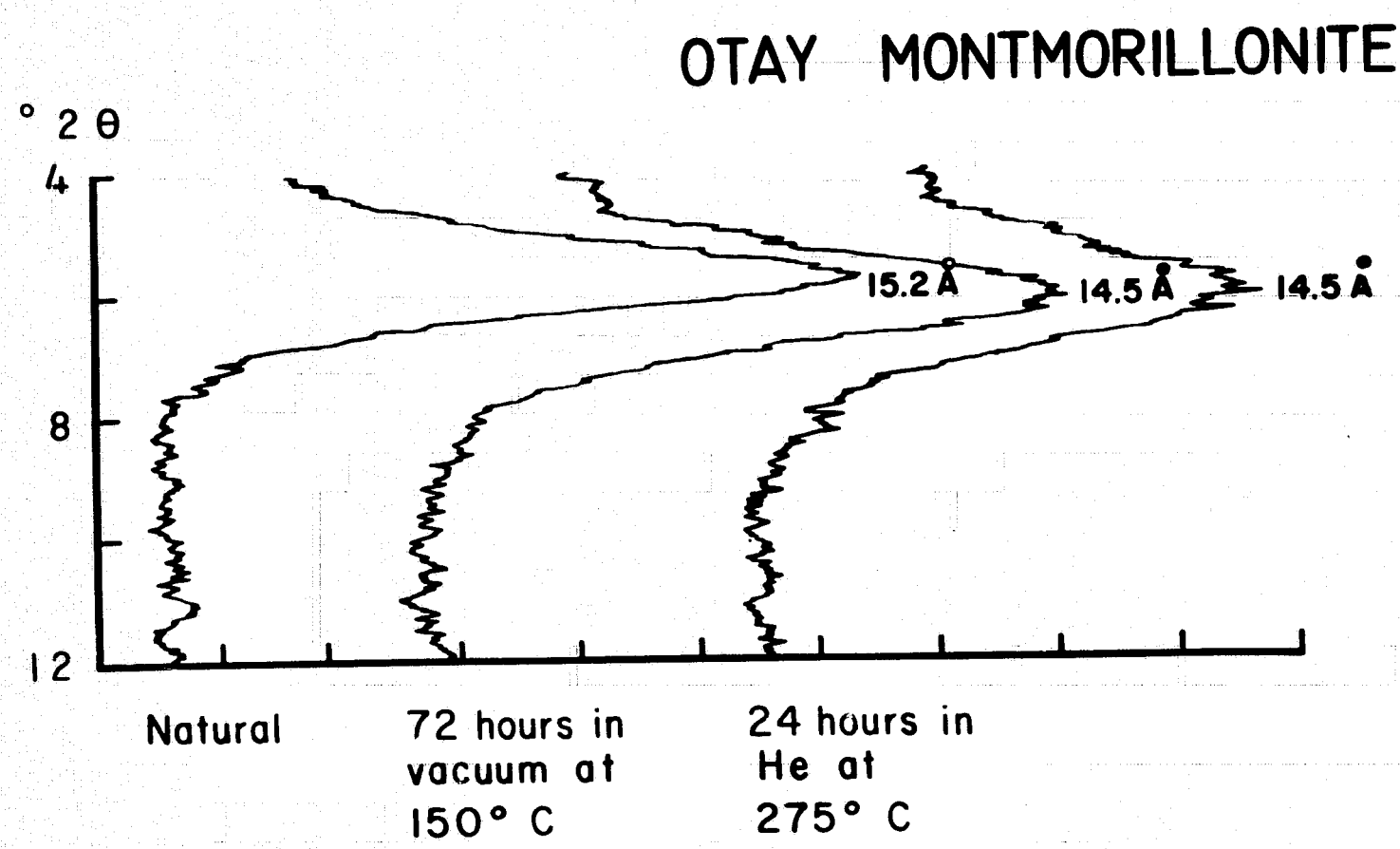


Figure 6. Tracings of x-ray powder diffraction patterns of the natural and heat treated samples of the Otay Montmorillonite.

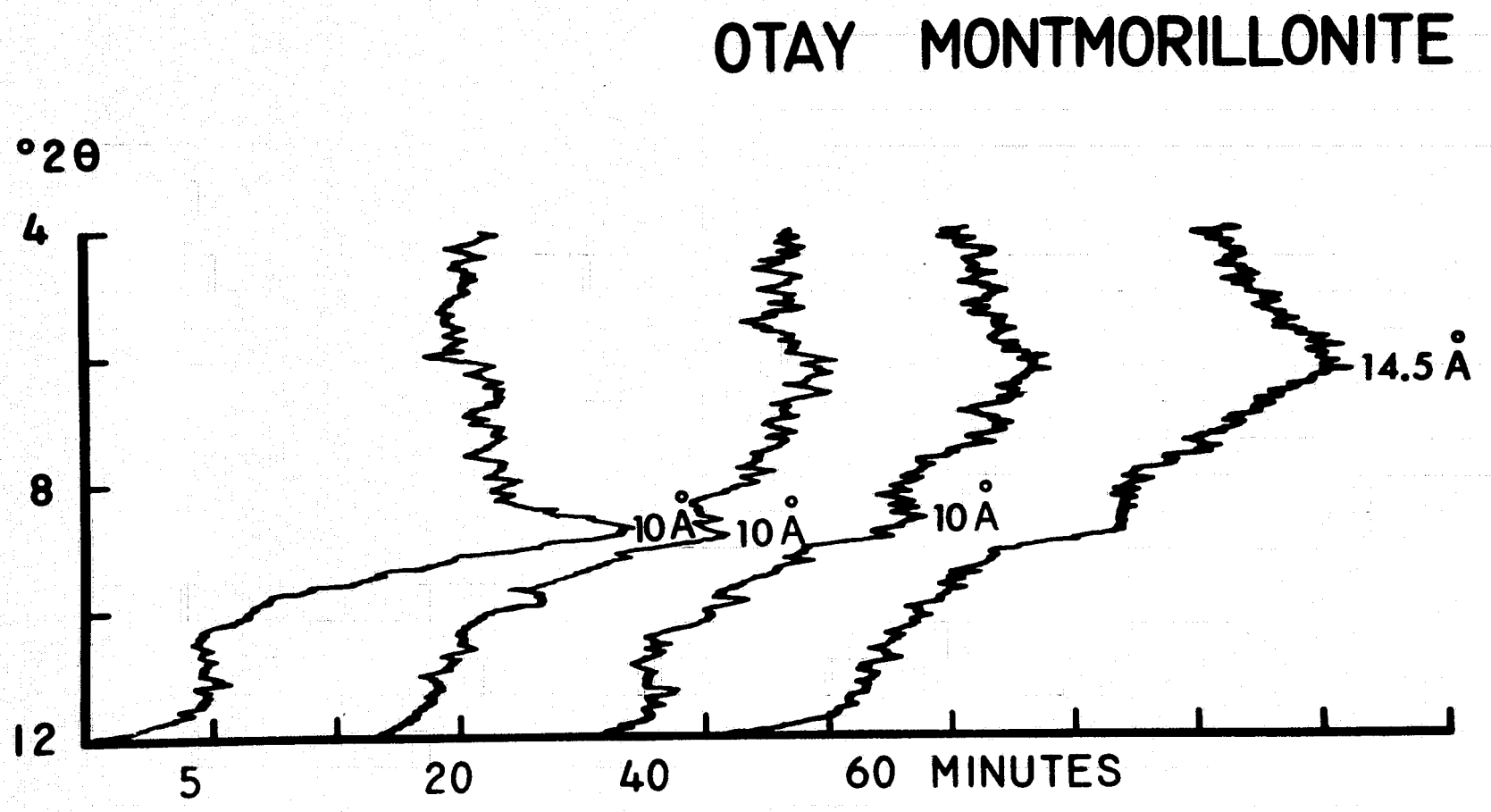


Figure 7. Tracings of x-ray powder diffraction patterns of samples of the Otay Montmorillonite made after 5, 20, 40 and 60 minutes.

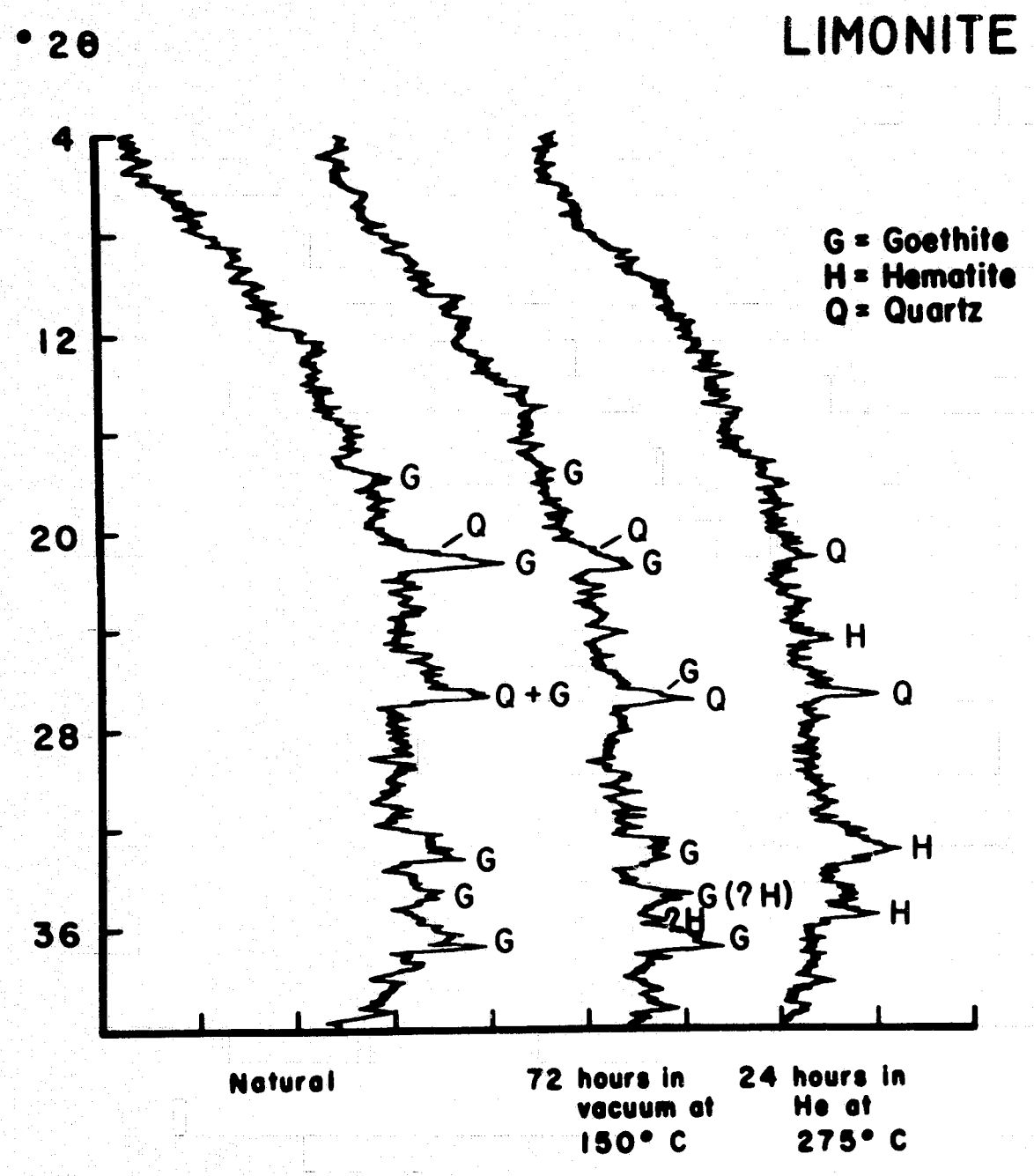


Figure 8. Tracings of natural and heat treated samples of Limonite.

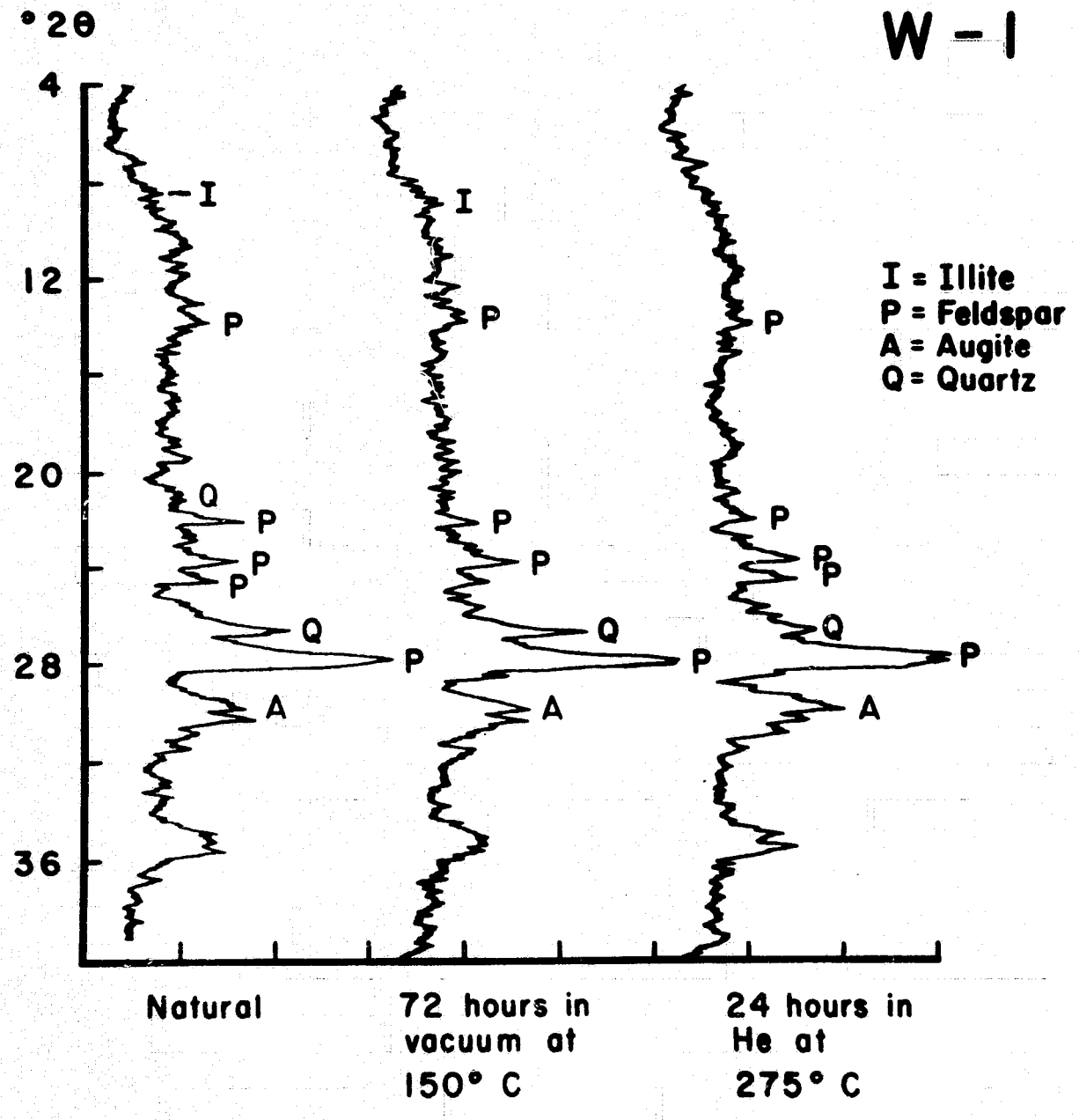


Figure 9. Tracings of x-ray powder diffraction patterns of samples of W 1.

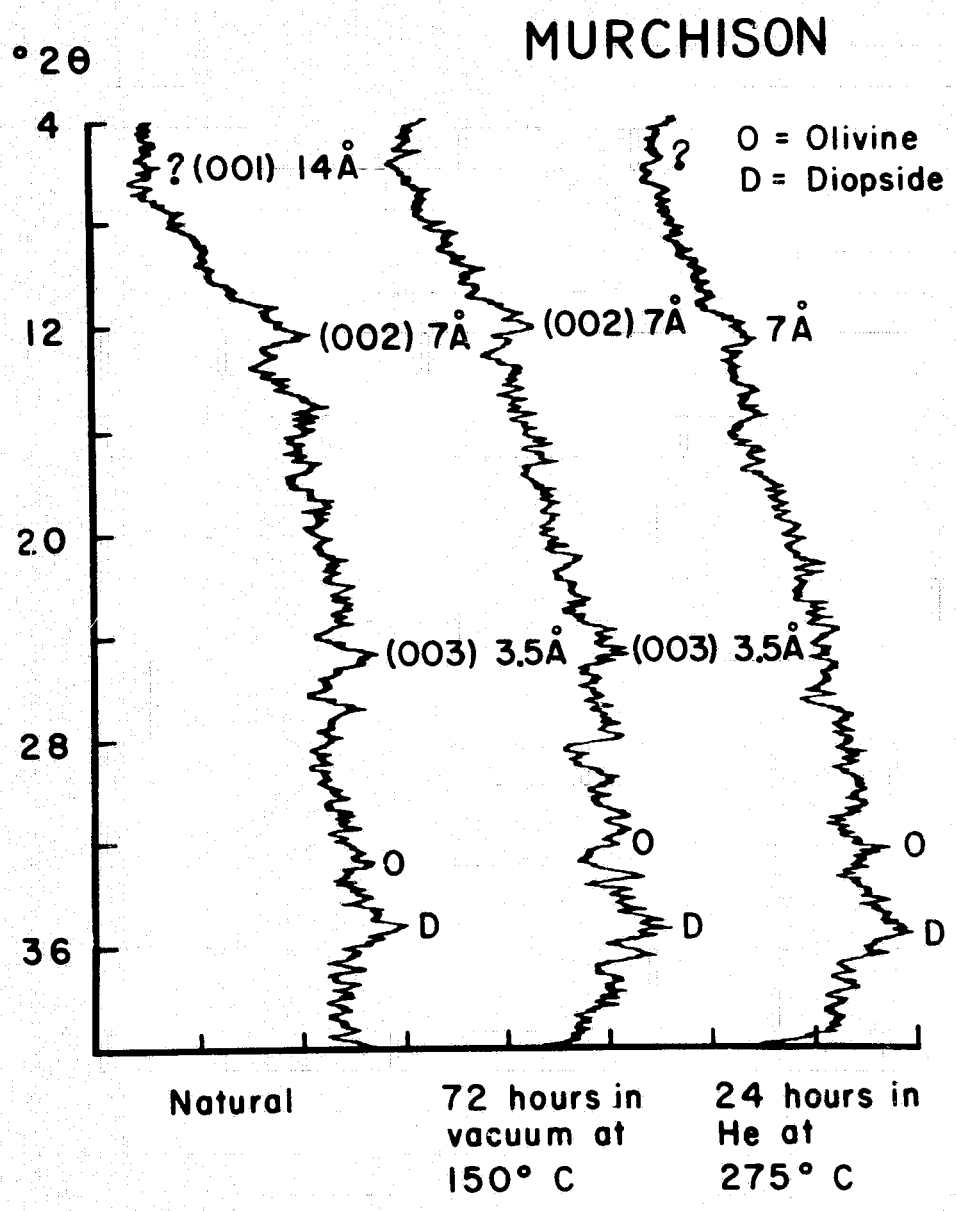


Figure 10. Tracings of x-ray powder diffraction powder patterns of natural and heat treated samples of Murchison meteorite.

Preliminary Mars Sample Study - effects of sample sterilization on data obtainable from x-ray powder diffraction

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March 1, 1974

Dr. Elbert A. King,
Dept. of Geology
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Houston, Texas 77004

Dear Elbert:

The heated and unheated test samples were run on the X-ray diffractometer using highly sensitive conditions and were studied on the electron microprobe using a solid-state detector with oscilloscope display. Ian M. Steele made the measurements. The results are partly obvious and partly not understood. Records and charts will be retained here unless you want to see them.

Limonite original: X-ray: amorphous + goethite + dioctahedral mica + quartz
heated: X-ray: hematite + mica + quartz

Therefore the goethite and amorphous phase (probably an iron oxide hydroxide gel) went to hematite. The mica and quartz were unchanged.

Montmorillonite original: X-ray: 14Å phase + quartz + unknown
s.s.d: qtz + K-feldspar + plag + apatite
heated: X-ray: 10Å phase + qtz + unknown
s.s.d: as above

Therefore the original montmorillonite is actually a mixture of many minerals with montmorillonite dominant. The montmorillonite lost its water upon heating as expected. The other minerals were unaffected.

Hesperia soil original: X-ray: quartz + plag + K-feldspar + unknown lines
s.s.d, quartz + plag + K-feldspar + amphibole?
heated: X-ray: quartz + plag + K-feldspar + unknown lines (not same as above)
s.s.d: quartz + plag + K-feldspar

Therefore the original soil is very complex with some X-ray lines not identified in routine study. The framework silicates retained their structures but the unknown phase(s) changed their structure.

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Murchisonite chondrite: original: X-ray: 7Å silicate + ? weak 14Å silicate + forsterite + enstatite + diopside + unknown

s.s.d. Mg,Fe silicates + FeS + Ca Mg Al Si silicate

heated: 7Å silicate (but lower proportion) + Fo + En + Di + unknown

Therefore the original assemblage (which is very complex, of course) retains most of its mineralogy except for the 7Å phase. Note the presence of a very weak 14Å line not recorded in the literature on carbonaceous chondrites.

W1: very simple, no changes detected by X-ray diffraction or solid-state detector.

Summary. These reconnaissance data confirm the expectations from existing mineralogic data, and confirm the statements in my letter to W. C. Phinney dated February 21. It is obvious that heat-treatment even at temperatures as low as 200-300° C will degrade the sample. If such temperatures are required for biological reasons it is important to carry out thorough experiments to find conditions which minimize damage. I want to emphasize that I would very much like to examine data from a heated sample: by careful thought, it should be possible to reconstruct the original mineralogy by use of combined diffraction, chemical and microprobe techniques. I am confident that we shall find that hematite obtained from limonite will have special morphological and chemical characteristics. It is important to monitor the gas released by heating.

Yours sincerely,

Joseph V. Smith

JVS/ib

copy: Dr. W. C. Phinney
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Preliminary Mars sample study - effects of sample sterilization on data obtainable from fluid inclusions

by

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March 4, 1974

ABSTRACT

A brief investigation was made of the effects of sterilization of 5 simulated Martian "soils" on the usefulness of such sterilized samples for fluid inclusion studies. Sterilization at 275°C for one day in helium at 1 atm. had almost no noticeable effect on the significance of the wide range of data available on the geological history of these samples that could be obtained from a study of their fluid inclusions. However, these results cannot necessarily be extrapolated to higher temperatures or to other types of sample materials.

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INTRODUCTION

On February 6, 1974, I was asked by Dr. E.A. King, Jr., of the University of Houston, to join in a preliminary group study of five simulated Martian soil samples. This effort was in response to a letter from Richard S. Young, Chief, Planetary Biology, Planetary Programs, Office of Space Sciences, pointing out the need to know the nature and magnitude of the impact of the sterilization procedure necessary for biological safety (the precise protocol of which is still under discussion) on the scientific results that might be obtained from study of a small sterilized sample of Martian soil. For this purpose I subsequently received two sets of 1-g samples of the following five simulated Martian "soils": Hesperia soil (a microbiological standard), limonite, montmorillonite, USGS standard diabase W-1, and the Murchison meteorite. One set was unheated, and the other (herein call "heated") was given a sterilization procedure assumed to be representative of that which will be needed for biological safety (heating at 275°C for 24 hours in helium at one atm.).

SIGNIFICANCE OF FLUID INCLUSION STUDIES TOWARD UNDERSTANDING THE PLANETARY EVOLUTION OF MARS

Fluid inclusions are minute portions of the fluid medium (silicate melt, aqueous brine, dense supercritical CO_2 fluid, etc.) from which most natural crystals have grown, trapped within crystals during their growth. As they are small (most are <10μm in size and $<10^{-10}$g in mass), and are usually abundant, they are preserved even in finely divided materials. They can provide a wealth of data on the P, T, and X of the environment(s) in which their host minerals formed, be they shallow volcanic or deep intrusive, high or low temperature metamorphic, or sedimentary. The inclusions in many terrestrial materials provide evidence of a sequence of different geological environments in the history of the sample, in the form of primary and secondary inclusions in the same grain, with grossly different fluid compositions and homogenization temperatures recording the two environments. It seems likely that a returned Martian soil sample would provide similar data. In fact, the Martian surface processes of physical and chemical weathering and mixing, and the resultant small grain to be expected in any returned Martian soil sample, combine to make a study of the fluid inclusions present a very important and necessary part of the overall investigation.

The optical procedures used in fluid inclusion studies, and their significance and applicability, have been summarized by Roedder (1972). It is most important to note here that as with any phase study, the genetic significance of a single fluid inclusion a few micrometers in

diameter, and hence weighing only $\sim 10^{-12}$g, is just as great as that of a million of them, in terms of understanding the geological history and environment on Mars. Most fluid inclusion techniques yield qualitative or semiquantitative data, but they frequently provide data otherwise unobtainable, and they can be used with very small samples. In addition, many are non-destructive.

The potentially most important data to be obtained from Martian fluid inclusions can be categorized as follows:

1. Composition of the fluid that was trapped. This may be an aqueous salt solution (varying from essentially pure water to saline melts), dense supercritical or liquified gases such as CO_2, silicate melts (or their crystallized equivalents), sulfide melts, etc. Such compositional data provide valuable insight as to the geological environments from which various grains in the sample may have come. Aqueous solution salinities can be obtained by the freezing stage method on as little as 10^{-11}g of solution (Roedder, 1962), and electron microprobe analyses can be made of silicate melt inclusions (e.g., Roedder and Weiblen, 1970, p. 810).

2. The pressure at the time of trapping. This may be estimated from the degree of filling of the inclusions and independent geothermometers, or a minimum value can be obtained from the inclusions alone, and then converted to depth of origin in the Martian gravity field.

3. The presence of noncondensable gases in inclusions. These can be detected using the crushing stage (Roedder, 1970). Although this is

a relatively simple technique, it is extremely sensitive, as the detection limit is only 10^{-14}g (i.e., 10^9 molecules). It will also yield some information on the gross composition of the gases.

4. The temperature of the environment at the time of trapping. This is determined by modern versions of the method of homogenization of the phases present, first used by Sorby (1858), with appropriate corrections. It is the aspect of inclusion work most subject to possibly serious effects from the sterilization procedures. The problem in evaluating the possible effects stems from the combination of the unspecified nature of the samples and the unspecified sterilization procedures to be used. Thermometry of lava flows from silicate melt inclusions will almost certainly be unaffected by any reasonable sterilization procedure. Extensive studies by many investigators show that aqueous fluid inclusions trapped at temperatures above that used for the sterilization can also be expected to be almost unaffected. The possibility of serious effects from sterilization (particularly decrepitation and loss of the inclusions) is much greater if the sterilization temperature is appreciably greater than the homogenization temperature (i.e., the inclusions are overheated), particularly with large inclusions (over 10 micrometers). This is a result of the high internal pressures that develop and cause stress in the walls. Small inclusions (<10μm), in hard minerals (such as quartz), can stand much more overheating than large ones in soft minerals such as calcite. The compressibilities of hot water solutions are such that those inclusions homogenizing at the lowest temperatures build up the

highest pressures on overheating. Thus an aqueous inclusion that homogenizes at 100°C will develop 2500 bars internal pressure on overheating to 250°C, whereas one that homogenizes at 200°C will only develop 700 bars when overheated to 250°C. Fairly extensive Soviet studies (Khetchiov and Samoilovich, 1970), have shown that fluid inclusions even in hard minerals such as quartz will decrepitate with internal pressures over 800 bars.

EXPERIMENTAL TECHNIQUE

As all samples were in the form of powder, and as fluid inclusion techniques require optically clear particles preferably ~10μm or larger, I made most of my observations on acid-insoluble, elutriated coarse residues. This is not a necessity, but greatly simplifies the optical search for significant inclusions. A portion of each sample was boiled with 1:1 HCl for five minutes, quenched and diluted with distilled water, and elutriated repeatedly to obtain clean fragments, dried at 110° for one hour, and mounted in index liquids appropriate for the minerals to be studied. This process obviously eliminates carbonates and other acid-soluble phases that may well contain valuable information, but in the short time frame allotted from sample receipt to finished report, it was the only feasible procedure. For the same reason the data obtained are all qualitative (quantitative studies would be vastly more time-consuming) but I believe they are quite adequate to answer the questions asked.

RESULTS OBTAINED

Although all ten samples were examined, most of the effort (and all of the photomicrography except as noted) was on the heated samples, because fluid inclusions generally either survive a heating unaffected, or decrepitate and are lost completely; only rarely are there effects of intermediate magnitude that may yield spurious data (Larsen et al., 1973), and these conditions are not likely in the acid insoluble samples*/. Photomicrography is an important part of the documentation of most inclusion studies, and it is unfortunate that the reproduction technique used for this report will not permit good halftones. The photomicrographs used here have been chosen with this in mind, but if glossy prints are needed, they can be supplied. Details on each photomicrograph are given where they fit in the text and are not duplicated in the figure captions. In all photomicrographs, V = vapor phase or "bubble"; L = liquid phase (generally a saline solution); G = glass (quenched silicate melt); H = host crystal.

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*/Another exception involves possible daughter crystals in aqueous inclusions, crystallized from the enclosed solution. Once these are redissolved (as by the sterilization procedure), they may not reform on cooling. Such metastability is common in these small systems (Roedder, 1971). As no such daughter phases were found in the brief examination of the unheated samples, this phenomenon could not be checked by these runs.

Hesperia soil

(A microbiological standard sample)

This soil contains a wide variety of types of mineral grains, evidentally from a range of geological environments, including intrusive igneous, near-surface volcanic, sedimentary, and metamorphic. The volcanic fragments include plagioclase with primary melt inclusions (now silicate glass, each with a shrinkage bubble; Fig. 1). Although this is a heated sample, there is not visible devitrification of the glass, nor would it be expected at 275°C. An electron microprobe analysis made on a section cut through these inclusions (e.g., Roedder and Weiblen, 1970, p. 810) would yield the composition of the quenched lava flow from which this crystal formed. Sequential laboratory heating experiments on such grains (Roedder and Weiblen, 1970, Fig. 7) could yield the temperature of crystallization of the flow and the sequence of phases formed, which delineates the magmatic differentiation trend (the liquid line of descent) that would be expected from such lavas. Other types of heating runs could yield some crude limits on the cooling rates for the original Martian flows (Roedder and Weiblen, 1971, Fig. 12).

Other grains of plagioclase in this sample, presumably from other flows, have silicate melt inclusions recording slower cooling rates (or perhaps melt compositions that nucleate and crystallize easier, or both). Fig. 2 shows two devitrified melt inclusions (presumably basaltic since the daughter crystals formed within them are opaque (oxide ?) phases) in a plagioclase crystal under partially crossed

nichols. Although no exactly equivalent grain was found in a brief examination of the unheated sample, I am certain that they do exist, and that this crystallization is not from the sterilization procedure.

Aqueous inclusions, each with a vapor bubble from shrinkage, are common in the quartz grains of igneous and metamorphic origin in this sample. Inclusions of water solution (salinity not determined) with moderately large bubbles such as Fig. 3 occur in both heated and unheated samples, and are obviously from moderately high temperature environments (intermediate metamorphic or late stage igneous). As a result of the large bubble, inclusions such as Fig. 3 are not expected to be affected by 275°C temperatures.

Inclusions with small bubbles are much easier to decrepitate, but I found that inclusions with small bubbles had indeed survived the heating. Fig. 4a, b is a composite of two photographs of the same quartz grain from the heated sample, taken in sequence at high magnification under optically difficult conditions to show the rapid "Brownian" (actually pseudoBrownian) movement of the vapor bubble in its cavity (arrows). This proves that it is indeed a liquid and not glass. I would guess that such inclusions would homogenize well below 150°C. There is an all-gas inclusion visible also (V). Such gas inclusions are probably dense CO_2 gas, but time did not permit verification.

A 55μm long zircon crystal found in the unheated sample contains a particularly large gas inclusion, also probably CO_2 (Fig. 5); equivalent grains were not seen in the small portion of the heated sample

that was scanned, but such inclusions should also be unaffected by 275°C. (Such zircons could also provide much valuable geological data, entirely apart from their fluid inclusions.)

Limonite

(Yellow ocher, Cartersville, Ga.; from Ward's Natural Science Establishment).

There was very little acid insoluble residue here, but the few grains of chert and detrital (?) quartz did contain aqueous inclusions, even after heating (Fig. 6). These inclusions probably reflect the environment of formation of the material that was weathered to produce this limonite. Crystals of carbonate, completely embedded in quartz and hence untouched by the acid, are also visible.

Montmorillonite

(Otay, Calif.; from Ward's Natural Science Establishment)

Four types of inclusions were found in the acid-insoluble detritus in the heated sample, and similar material was present in the unheated material. First, the quartz host around some solid mineral inclusions (Fig. 7) was found to exhibit stress birefringence due to change in P and/or T. With adequate care, such stress birefringence can be used to estimate (or place limits on) the pressure and temperature of the environment of crystallization (Rosenfeld, 1969).

A 76-μm zircon crystal, with a gas inclusion, was found (Fig. 8). This is presumably also an inclusion of relatively low-pressure CO_2, but has not been checked further.

One grain of kyanite (presumably from a metamorphic terrain) contained moderately large CO_2 inclusions (Fig. 9), and a grain of quartz (Fig. 10) showed many inclusions with a low volume percent vapor phase, corresponding to ~150-200°C homogenization temperatures.

Diabase (U.S.G.S. standard W-1)

Very few inclusions are visible in this material. The only mineral that happens to have been effective in trapping inclusions is the late quartz, which makes up only 1.8 weight percent (Chayes, 1951). It contains relatively rare low density gas inclusions (presumably formed during near-surface cooling) in the unheated material (Fig. 11), and similar all-gas inclusions, though not as photogenic (Fig. 12), were found in the heated sample. Much more significant to the problems posed here are the rare dense (small vapor bubble) aqueous inclusions also found in this quartz in the unheated sample. These are probably formed from deuteric solutions during still later, near-surface cooling. After much search, several of these in the 1.5-2μm diameter range were found in the heated sample, but almost impossible to photograph. One last mount, however, revealed the "large" 11-μm aqueous inclusion seen in Fig. 13, so some such inclusions can survive the sterilization, although most have probably decrepitated.

Murchison meteorite (a carbonaceous chondrite)

Although I have already spent considerable time studying the inclusions in this meteorite (unpublished work), the present samples

provided better examples of several types of inclusions than all the previous work. Many are melt inclusions, trapped at high temperatures, in olivine or pyroxene. None had visibly devitrified, even faintly. These are primary inclusions, trapped during the growth of the host olivine in that never-never land where meteorites originate. Fig. 14 shows a particularly good glass inclusion in olivine, with its small shrinkage bubble. Some of these glass inclusions were attached to spinel crystals embedded in the olivine, proving their very early origin, during the growth of the host olivine from the melt. One crystal of orthopyroxene (in the heated sample) contains melt inclusions with very large bubbles (Fig. 15). Although the usual interpretation of the bubbles in inclusions is that they form by thermal shrinkage on cooling, and hence inclusions with large bubbles formed at very high temperatures, it is more likely that these formed from a melt containing a large amount of normative pyroxene, which crystallized out on the walls during cooling (Roedder and Weiblen, 1973, p.1049). The vapor bubble would then correspond to the sum of a large ΔV from crystallization of a large volume of pyroxene onto the walls, plus a small ΔV from the thermal shrinkage of the remaining melt.

Some evidence for low pressure gas (possibly CO_2?) was also found. Thus Fig. 16 shows a grain of olivine containing normal silicate melt inclusions with a shrinkage bubble, and an "empty" gas inclusion at V.

This same grain, at a different level of focus (Fig. 17) (as well as many others), shows evidence of separation of an immiscible, opaque $melt_A^{(S)}$ from the silicate melt in the inclusions after trapping. This is

presumably an immiscible iron sulfide melt, similar to that found in inclusions of olivine in many lunar basalts (Roedder and Weiblen, 1970, pp. 805 and 809), and provides evidence of saturation of the melt with respect to FeS; from the relative volumes of the sulfide globule and silicate melt one may obtain the change in solubility of FeS with temperature.

One additional type of inclusion that is relatively abundant in the Murchison meteorite results from the early separation of immiscible blebs of liquid metallic iron (M) in the silicate melt from which these olivines grew. Figs. 18, 19, and 20 illustrate a series of such inclusions. In Fig. 18 there are two metallic iron blebs enclosed in olivine, one with a small amount of silicate melt, now glass (G), and a vapor (shrinkage) bubble (V). There is also a normal melt inclusion between these two. Fig. 19 shows a similar inclusion with a different metal/silicate ratio, and Fig. 20 shows a particularly large one (all of 22.7μm long). From examination of many such inclusions, it is evident that the vapor bubble represents a combination of three sources of volume decrease in this tiny closed system: ΔV from crystallization of olivine on the walls, ΔV from crystallization of the iron sphere, and ΔV from shrinkage on cooling of the trapped silicate melt.

None of the above features seem to have been influenced in the slightest by the sterilization procedures, as identical inclusions are found in the unheated sample.

DIRECTIONS FOR FUTURE INCLUSION RESEARCH

Several avenues of investigation are rather obvious from the preceding results. In view of the possibility of carbonate minerals (formed at low temperatures) being present in the Martian soils, the effects of sterilization on the inclusions in such materials should be investigated, particularly when the possible ranges of sterilization variables have been narrowed appreciably. The behavior of very low temperature inclusions (<150°C) in both hard and soft minerals should likewise be studied. Other types of sample material should also be used, in particular a fresh basalt (as contrasted with the chloritized diabase sample W1) and one or more metamorphics, as well as basaltic and rhyolitic pyroclastic material.

CONCLUSIONS

Within the limits of this brief examination, the sterilization protocol used in this preliminary trial run (275°C, 1 day, in helium at one atm) has almost no noticeable effects on the fluid inclusions present in these materials. These results cannot necessarily be extrapolated to higher temperatures or to other types of sample materials. For example, liquid CO_2 inclusions, which are commonly found in terrestrial samples, develop such large internal pressures on overheating that only the olivine structure seems capable of containing it (Roedder, 1965, p. 1770), and aqueous inclusions in soft minerals such as calcite that homogenize as temperatures below that of the sterilization may leak or decrepitate and be lost. Within such limitations, however, it appears that most if not all of the science that can be done on Martian samples via fluid inclusion studies can be done just as well on sterilized samples. If the Martian soil contains detritus larger than a minimum of ~10μm, from the mechanical or chemical weathering of rocks similar to those on earth or Moon, or to meteorites, a large amount of otherwise unobtainable qualitative and some important quantitative data can be derived from even relatively simple microscopy of the fluid inclusions in very small samples, after sterilization for 1 day in helium at 275°C. Additional valuable compositional data can be obtained on silicate melt inclusions when the microscopy and laboratory heating experiments are combined with subsequent electron microprobe studies. The total amount of material used from any sample in the present tests was <1-mg, and as these tests are nondestructive,

it could be recovered with the only contamination being from contact with organic index liquids.

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Photomicrographs

All taken in transmitted plane polarized light except as noted. The bar on each photograph represents 10 μm except Figs. 3 and 19, where it represents 5 μm.

Fig. 1. Hesperia soil (heated). Plagioclase with glass inclusions.

Fig. 2. " " " Plagioclase with devitrified melt inclusions (partially crossed nichols).

Fig. 3. Hesperia soil (heated). Quartz with aqueous inclusion.

Fig. 4. " " " " with aqueous inclusions and moving vapor bubbles (arrows), and a vapor inclusion (V).

Fig. 5. Hesperia soil (unheated). Zircon crystal with large gas inclusion.

Fig. 6. Limonite (heated). Quartz with aqueous inclusion.

Fig. 7. Montmorillonite (heated). Quartz with solid inclusions.

Fig. 8. " " Zircon crystal with gas inclusion.

Fig. 9. Montmorillonite (heated). Kyanite with CO_2 inclusion.

Fig. 10. " " Quartz with aqueous inclusions.

Fig. 11. Wl (unheated). Quartz with gas inclusion.

Fig. 12. " (heated). Quartz with gas inclusion.

Fig. 13. Wl (heated). Quartz with aqueous inclusion.

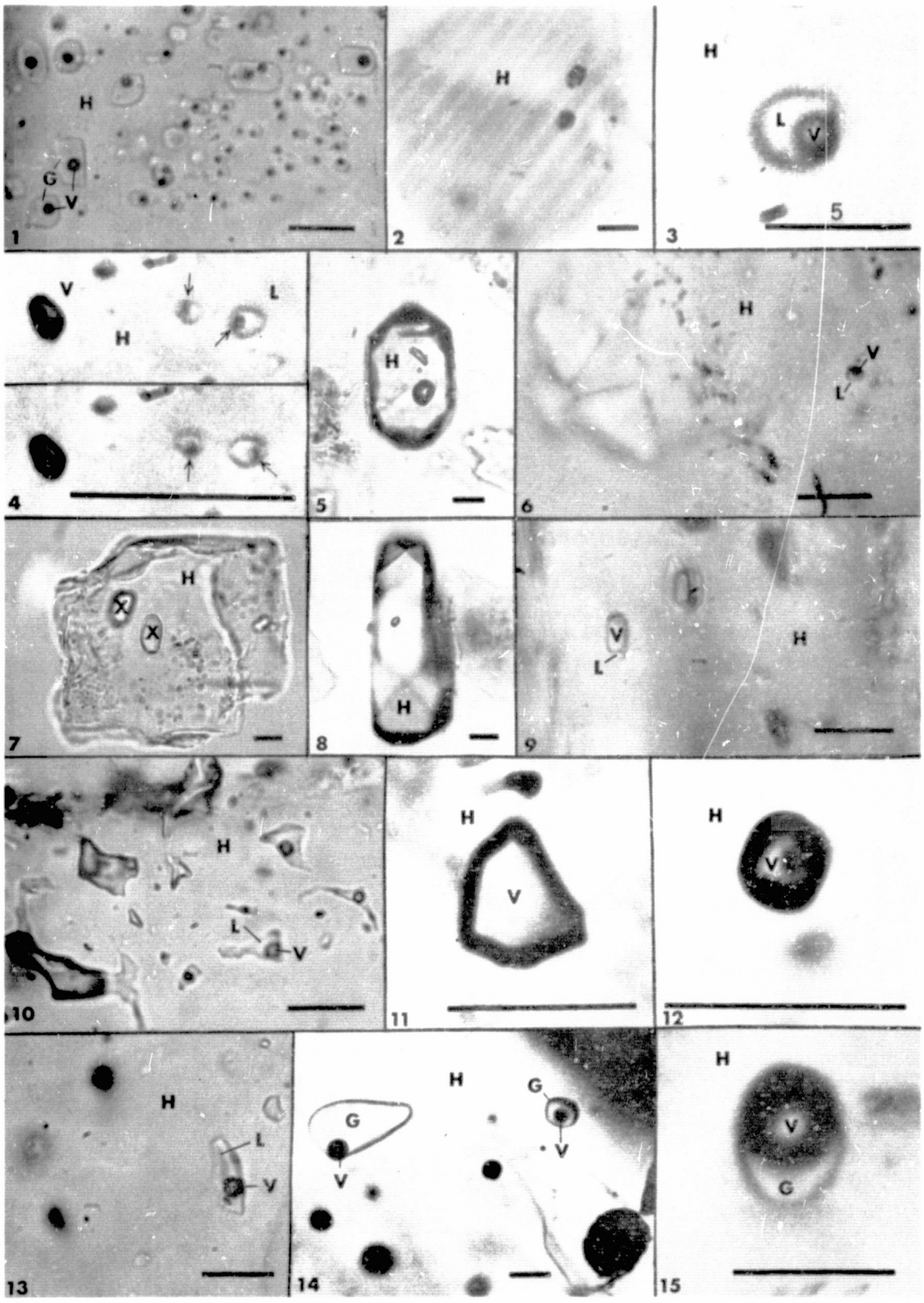
Fig. 14. Murchison (heated). Olivine with glass inclusions and many opaque metallic iron globules.

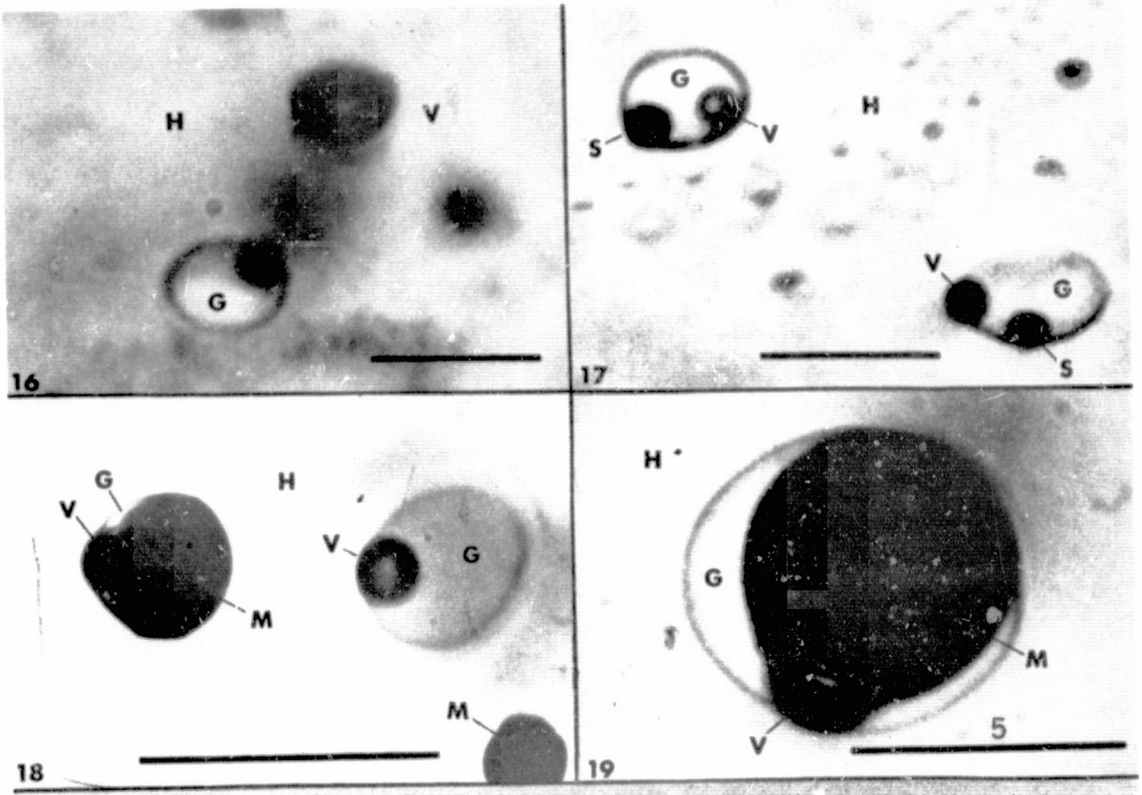
Fig. 15. Murchison (heated). Orthopyroxene with glass inclusion.

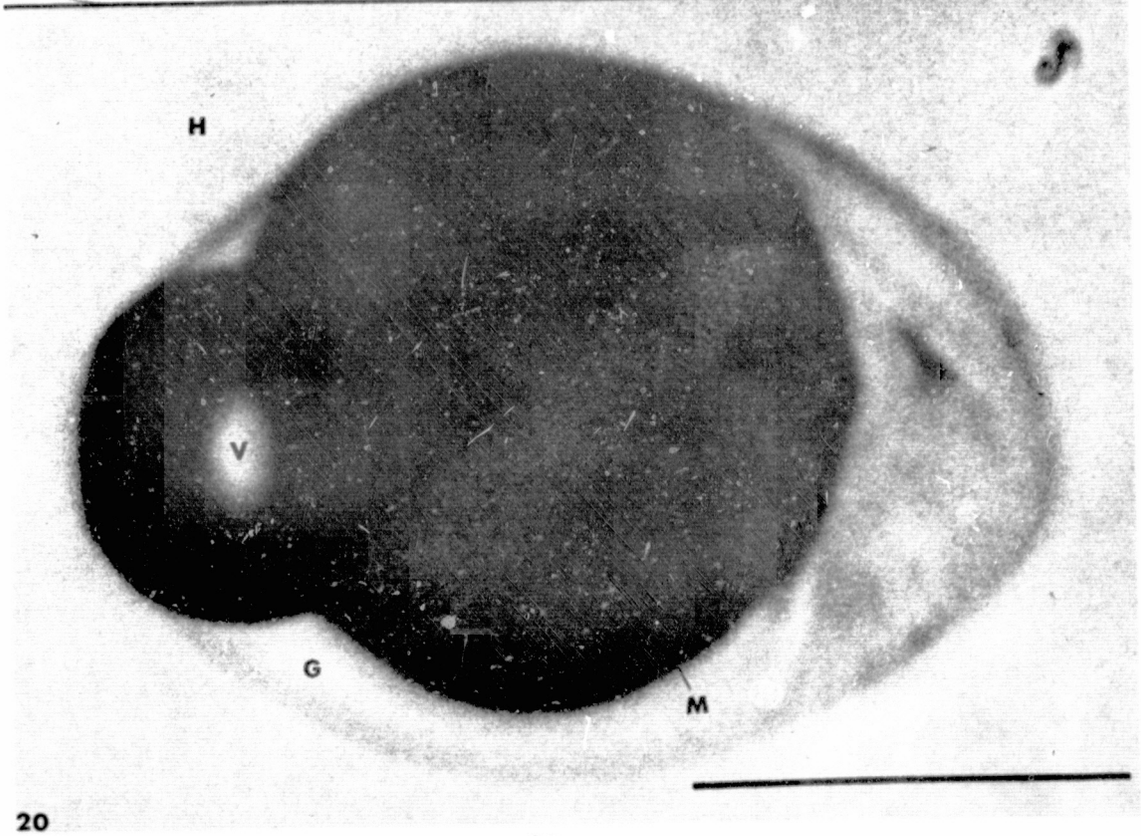
Fig. 16. " " Olivine with gas inclusion (V) and glass inclusion.

Fig. 17. Murchison (heated). Olivine with glass inclusions containing exsolved sulfide droplets (S).

Figs. 18-20. Murchison (heated). Olivine with iron globules (M) and silicate glass (G) with vapor bubble (V).


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Preliminary Mars Sample Study - chemical analysis of selected samples

Pratt Johnson

NASA, JSC and The University of Houston
Houston, Texas

The following analytical data for major elements and some trace elements were obtained by optical emission spectroscopy and atomic absorption spectrophotometry using the methods developed for the analysis of lunar samples in the NASA JSC Lunar Receiving Laboratory. Documentation of the analytical methods can be found in the Lunar Receiving Laboratory Operating Procedures (Curator's Office, JSC) or methods descriptions can be obtained by contacting me personally.

Due to the short time available for the analysis, all data should be considered as preliminary.

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CHEMICAL ANALYSIS OF LIMONITE*

Element	Natural	Heated at 275°C for 24 hours
SiO_2	13.7 g/100g	17.1 g/100g
Al_2O_3	7.50	7.41
Fe_2O_3	36.1	36.9
MgO	0.85	0.96
CaO	0.81	0.88
Na_2O	———	———
K_2O	0.95	1.30
TiO_2	0.64	0.49
P_2O_5	2.2	1.8
MnO	0.67	0.82
Cr_2O_3	0.015	0.01
B	3.1 ug/g	4.5 ug/g
Ba	2458	2754
Be	17	14
Co	148	150
Cu	110	94
La	424	540
Ni	829	919
Sc	37	17
Sr	390	280
Th	13	6.7
V	152	160
Y	25	26
Yb	16	18
Zr	158	122

* Pratt Johnson JSC and University of Houston

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CHEMICAL ANALYSIS OF STANDARD W 1

Element	Natural	Heated at 275°C for 24 hours
SiO_2	54.2 g/100g	50.9 g/100g
Al_2O_3	15.3	15.3
Fe_2O_3	10.9	11.7
MgO	6.23	6.84
CaO	10.9	11.0
Na_2O	2.0	2.32
K_2O	———	———
TiO_2	1.45	1.43
P_2O_5	0.7	0.8
MnO	0.19	0.20
Cr_2O_3	0.02	0.03
B		0.004 ug/g
Ba	145	176
Be	1.8	1.8
Co	40	50
Cu	117	131
La	13	10
Ni	83	35
Sc	47	29
Sr	56	59
Th	4.0	1.3
V	211	136
Y	22	25
Yb	1.3	1.3
Zr	172	164

*Pratt Johnson JSC and University of Houston

CHEMICAL ANALYSIS OF HESPERIA SOIL

Element	Natural	Heated at 275°C for 24 hours
SiO_2	57.4 g/100g	60.6 g/100g
Al_2O_3	20.8	18.1
Fe_2O_3	7.19	6.68
MgO	3.04	2.24
CaO	4.71	4.85
Na_2O	2.42	3.35
K_2O	2.47	2.45
TiO_2	1.22	1.02
P_2O_5	0.3	0.3
MnO	0.14	0.11
Cr_2O_3	0.02	0.06
B	1.4 ug/g	1.6 ug/g
Ba	1100	831
Be	1.7	1.2
Co	8.3	8.7
Cu	16	32
La	33	15
Ni	5.8	4.4
Sc	25	15
Sr	292	219
Th		12
V	76	80
Y	34	26
Yb	3.1	1.8
Zr	775	727

* Pratt Johnson JSC and University of Houston

CHEMICAL ANALYSIS OF THE MURCHISON METEORITE*

Element	Natural	Heated at 275°C for 24 hours
SiO2	28.0 g/100g	26.5 g/100g
Al_2O_3	3.01	3.84
Fe_2O_3	25.8	34.7
MgO	19.2	27.8
CaO	1.5	2.14
Na_2O	0.009	0.16
K_2O	———	———
TiO_2	0.20	0.25
P_2O_5	1.7	1.8
MnO	0.26	0.30
Cr_2O_3	0.78	1.06
B		0.004 ug/g
Ba	17	19
Be	0.5	0.5
Co	527	603
Cu	202	138
La	38	29
Ni	6788	7715
Sc	12	93
Sr	40	66
Th	27	7.9
V	53	54
Y	21	24
Yb	1.3	2.3
Zr	67	73

* Pratt Johnson JSC and University of Houston

CHEMICAL ANALYSIS OF THE OTAY MONTMORILLONITE *

Element	Natural	Heated at 275°C for 24 hours
SiO_2	61.0 g/100g	57.1 g/100g
Al_2O_3	19.0	20.6
Fe_2O_3	3.07	3.28
MgO	8.11	9.20
CaO	1.08	1.16
Na_2O	1.17	1.29
K_2O	—	—
TiO_2	0.60	0.58
P_2O_5	0.1	0.1
MnO	0.19	0.14
Cr_2O_3	0.008	0.004
B	1.3 ug/g	1.3 ug/g
Ba	353	366
Be	2.0	2.8
Co	0.3	0.03
Cu	37	
La	15	40
Ni	2.7	6.7
Sc	7.0	7.3
Sr	76	114
Th	13.9	21
V	41	55
Y	51	53
Yb	2.4	3.1
Zr	347	487

* Pratt Johnson JSC and Univeristy of Houston

Preliminary Mars Sample Study - Uranium, Lead and Thorium analyses

M. Tatsumoto

U. S. Geological Survey
Denver, Colorado

All analytical data should be considered as preliminary because of the very short time available for the analyses.

The data include total amounts of uranium, thorium and lead present only, and do not make any statement concerning the distribution of these elements and their isotopes between the various mineral phases present.

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URANIUM, LEAD AND THORIUM ANALYSIS OF NATURAL AND HEATED SAMPLES OF W 1 AND MURCHISON[a]

Sample	Wt. mg	Observed*		
		$\frac{206\ Pb}{204\ Pb}$	$\frac{207Pb}{206Pb}$	$\frac{208Pb}{206Pb}$**
W 1 Natural	449.5	18.642	0.83886	2.0807
W 1 Heated at 275°C for 24 hours	597.0	18.656	0.83818	2.0807
Murchison Natural	454.6	10.279	1.0591	3.039
Murchison Heated at 275°C for 24 hours	477.2	10.159	1.0648	3.039

a Tatsumoto

Sample	Corrected for Blank		
	$\frac{206\ Pb}{204\ Pb}$	$\frac{207Pb}{206Pb}$	$\frac{208Pb}{206Pb}$
W 1 Natural	18.642 .012***	0.83884 .00041	15.638
W 1 Heated at 275°C 24 hours	18.656 .011	0.83817 .00035	15.637
Murchison Natural	10.260 .031	1.0600 .0019	10.875
Murchison Heated at 275°C for 24 hours	10.140 .036	1.0657 .0019	10.806

* Corrected for 208 "spike" and fractionation

** 208Pb/206Pb data for W 1 from BCR, Tatsumoto et al., U.S.G.S. Prof. Pap., 800-D, pp D111-D115, 1972; For Murchison, Tilton, E.P.S.L. v. 19, no. 3, pp. 321-329, 1973.

*** to be read as "plus or minus".

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URANIUM, LEAD AND THORIUM ANALYSIS OF NATURAL AND HEATED SAMPLES OF W 1 AND MURCHISON

Sample	Uranium	Thorium	Lead	232Th/238U
W 1 Natural	0.5777ppm .0045*	2.327ppm .009	6.405ppm .068	4.162
W 1 Heated at 275°C - 24 hours	0.5907 .0046	2.180 .008	6.393 .059	3.812
Murchison Natural	0.0196 .0004	0.0771 .0003	1.647 .016	4.057
Murchison Heated 275°C - 24 hours	0.0202 .0004	0.0725 .0003	1.650 .016	3.702

* to be read as "plus or minus"

Preliminary Mars Sample Study - weight loss studies; analysis for sodium, rubidium and lithium

J. A. Philpotts
D. F. Nava
S. R. Winzer
R. Lum

N.A.S.S.
Astrochemistry Branch
Goddard Space Flight Center
Greenbelt, Maryland

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND 20771

FILE 12377

MAR 1 '74

REPLY TO ATTN OF: Code 691

Dr. Elbert King
Dept. of Geology
University of Houston
Houston, Texas 77004

Dear Elbert:

Enclosed please find analytical data obtained by my colleagues D. F. Nava, S. R. Winzer, and R. Lum for your "Mars" samples. Hope they are in suitable form. See you at the Conference.

All the best,

John

John A. Philpotts
Astrochemistry Branch

c.c. E. Gibson

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND 20771

REPLY TO
ATTN OF:

Weight Change and Sodium Determinations on "Mars Analog" Materials

Analytical Chemist: D. F. Nava
Astrochemistry Branch

	% Weight Loss	% Sodium
USGS W-1		
Original Unheated	0.19	1.61
150°C in Vacuum	0.09	1.61
275°C in Helium	0.08	1.64
Murchison Meteorite		
Original Unheated	3.21	0.254
150°C in Vacuum	0.25	0.208
275°C in Helium	1.21	0.247
Otay Montmorillonite		
Original Unheated	13.54	1.00
150°C in Vacuum	0.64	1.14
275°C in Helium	1.17	1.18
Limonite		
Original Unheated	0.43	0.014
150°C in Vacuum	0.54	0.015
275°C in Helium	0.62	0.016
Hesperia Soil		
Original Unheated	1.85	2.10
150°C in Vacuum	0.56	2.25
275°C in Helium	0.67	2.16

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Discussion of Results

Of the results obtained for the weight change (a loss of weight in all cases) and the sodium determinations on these "Mars analog" materials, the only clear trend is that the heated samples treated under vacuum at 150°C have been found to be, except for limonite, "drier" or more free of low temperature volatiles than the unheated original samples or than the 275°C helium heated samples. This may be due to the vacuum environment enhancing the effective vapor pressure and removal of such volatiles (including water) while the heat treatment under a pressure of helium atmosphere, even though at a higher temperature, retarded as extensive liberations of these volatiles; a type of mass-action effect of environmental pressure upon volatilization reactions.

In the case of the vacuum and helium "sterilized" limonite samples exhibiting a higher weight loss than the original material, this weight change may be due to changes induced in the structure of the hydrous iron oxide which, when exposed to the air subsequent to the heat treatments, permitted uptake of a higher water abundance than that contained in the original material.

The relative changes in the sodium concentrations are not entirely consistent with the weight loss changes and thus imply a more complex effect(s) brought about by the "sterilization" treatments.

Based upon the sample preparation and handling information received (E. King, Univ. of Houston letter dated 2/6/74), other constituents were not determined because of probable various contaminations with Fe, Cr, Ni, Mn, Cu (from grinding with stainless steel) and/or with Al (from grinding in alumina).

Analytical Methods

Weight Change Determinations:

Gravimetric; determined on nominal one gram sample aliquants heated in platinum crucibles at 115°C for two hours (in air atmosphere). Reproducibility (i.e., precision) of analytical weighings + heatings + desiccations (based on replicate tares of crucibles and duplicates of original limonite) is within ± 0.0002 grams absolute, which is equivalent to ± 0.02 weight per cent change for a sample basis of one gram. Data is expressed as % weight loss.

Sodium Determinations:

Flame atomic absorption spectrophotometry; sample aliquants of nominal 250 milligram quantities prepared - thought to be reasonably representative split size. Sample decompositions via HF-aqua regia in closed teflon bombs followed by complexation with boric acid (after Nava & Philpotts, Geochim. Cosmochim. Acta Vol. 37, pp. 963-973, 1973). All samples were analyzed vs one set of co-element composite working atomic absorption standard solutions. Analytical precision, based on triplicates of the original W-1 sample is approximately 1.5% relative. Absolute abundances are not necessarily of highest accuracy since the five sample materials are chemically quite dissimilar and therefore in order to achieve highest analytical accuracy, would require, when analyzed via atomic absorption spectrophotometry, analysis as five separate sample sets, each with its own close-bracketing set of co-element composite working standards. (The same requirement would exist if determined by flame photometry, emission, because the same nebulization and flame processes would occur as for atomic absorption.) Relative comparisons, however, of sodium data among original and "sterilized" samples of each material are valid. Sodium data in the table is expressed as weight % Na.

David F. Dyke
March 14, 1974

MASS SPECTROMETRIC ISOTOPE DILUTION ANALYSES OF MONTMORILLONITE AND LIMONITE

Sample	PPM Rb	PPM Li
Montmorillonite (unheated)	30.2	137
Montmorillonite (heated 275°C)	35.3	165
Limonite (unheated)	44.3	27.9
Limonite (heated 275°C)	48.8	29.0

Analysts: S.R. Winzer and R. Lum

Percent change on heating

Montmorillonite	+17.0	+20.4
Limonite	+10.2	+ 3.9

Ratios

Sample	Li/Rb
Montmorillonite (unheated)	4.54
Montmorillonite (heated 275°C)	4.67
Limonite (unheated)	0.63
Limonite (heated 275°C)	0.59

Comment:

The increase in concentration of all elements is to be expected for the montmorillonite due to water loss on heating. All of the increase shown does not seem to be explained by water loss, however (see data of NAVA). Rb and Li increase in the limonite after heating

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even though a decrease would be expected from the water data. This increase is not consistent for both elements. These observations suggest that contamination may be responsible for some of the variations observed. It is difficult to ascertain the cause of such contamination from the data presented in the memo. Significant Fe and Al contamination can be expected from the proceedures used, but little Rb or Li contamination would be expected. Although the variations seen in these data may be due to the sterilization proceedure, the possibility of contamination makes discussion of the actual changes caused by sterilization of dubious validity.

Stephen R. Winzer

Stephen R. Winzer

Preliminary Mars Sample Study - weight loss studies and gas release curves of selected samples.

E. Gibson
G. Moore

NASA, JSC
Houston, Texas

For each sample analyzed there is a table indicating percent weight loss at each temperature on stepwise heating from 100°C to 1400°C. Also there is a set of gas release curves indicating the temperatures of gas releases in four different mass ranges and a total curve which includes all mass ranges.

For description of the technique used see papers in the Lunar Science Conference Proceedings from our laboratory.

WEIGHT LOSS DETERMINATIONS FOR STANDARD LIMONITE*

Temperature	% Weight Loss Natural	% Weight Loss 150°C in Vacuum	% Weight Loss 275°C in Helium
100° C	0.58%	0.26%	0.16%
200°	6.60	1.21	0.44
300°	7.18	5.60	0.64
400°	7.40	6.02	1.03
500°	7.58	6.28	1.30
600°	7.60	6.39	1.44
700°	8.07	6.58	1.63
800°	8.39	6.77	1.99
900°	8.92	7.30	2.37
1000°	9.77	8.06	2.94
1100°	11.51	10.06	4.72
1200°	12.09	10.78	5.38

* Gibson and Moore

See Figures 1, 2 and 3.

WEIGHT LOSS DETERMINATIONS FOR W 1*

Temperature	% Weight Loss Natural	% Weight Loss 150°C in Vacuum	% Weight Loss 275°C in Helium
100°C	0.03%	0.02%	0.00%
200°	0.08	0.04	0.04
300°	0.14	0.08	0.10
400°	0.22	0.17	0.20
500°	0.36	0.30	0.30
600°	0.42	0.38	0.34
700°	0.48	0.47	0.41
800°	0.56	0.55	0.47
900°	0.61	0.59	0.51
1000°	0.66	0.62	0.54
1100°	0.72	0.69	0.59
1200°	0.79	0.73	0.63
1300°	0.89	0.89	0.76
1400°	1.42	1.46	1.28

* Gibson and Moore

See Figures 4, 5 and 6.

WEIGHT LOSS DETERMINATIONS FOR MURCHISON METEORITE*

Temperature	% Weight Loss Natural	% Weight Loss 150°C in Vacuum	% Weight Loss 275°C in Helium
100°	0.84%	0.00%	0.44%
200°	2.11	0.42	0.68
300°	5.22	3.38	1.01
400°	7.96	5.16	3.34
500°	9.24	8.22	7.00
600°	10.12	9.44	9.02
700°	11.43	10.75	10.51
800°	12.27	11.97	11.63
900°	13.30	12.96	12.56
1000°	14.18	13.80	13.53
1100°	15.17	14.74	14.13
1200°	16.05	15.63	14.41
1300°	16.61	16.10	14.53
1400°	17.60	16.90	15.14

*Gibson and Moore

See Figures 7, 8 and 9.

WEIGHT LOSS DETERMINATIONS FOR OTAY MONTMORILLONITE*

Temperature	% Weight Loss Natural	% Weight Loss 150°C in Vacuum	% Weight Loss 275°C in Helium
100°C	0.95%	0.97%	0.42%
200°C	1.52	1.51	0.56
300°C	2.10	2.10	0.89
400°C	2.89	3.05	1.59
500°C	3.84	4.42	2.78
600°C	5.15	5.49	4.45
700°C	5.78	5.87	5.04
800°C	6.10	6.14	5.15
900°C	6.41	6.25	5.32
1000°C	6.57	6.38	5.38
1100°C	6.83	6.50	5.50
1200°C	6.99	6.66	5.62
1300°C	7.20	6.76	5.76
1400°C	8.04	7.11	6.08

* Gibson and Moore

See Figures 10, 11 and 12.

WEIGHT LOSS DETERMINATIONS FOR HESPERIA SOIL*

Temperature	% Weight Loss Natural	% Weight Loss 150°C in Vacuum	% Weight Loss 275°C in Helium
100°C	0.17%	0.00	0.21
200°C	0.69	0.07	0.37
300°C	1.32	0.54	0.86
400°C	2.06	1.04	1.47
500°C	2.74	1.40	1.96
600°C	2.84	1.83	2.25
700°C	3.06	1.96	2.40
800°C	3.23	2.13	2.53
900°C	3.45	2.30	2.69
1000°C	3.67	2.44	2.84
1100°C	4.31	2.76	3.03
1200°C	4.45	3.01	3.26
1300°C	4.89	3.33	3.58
1400°C	5.95	3.98	4.46

*Gibson and Moore

See Figures 13, 14 and 15.

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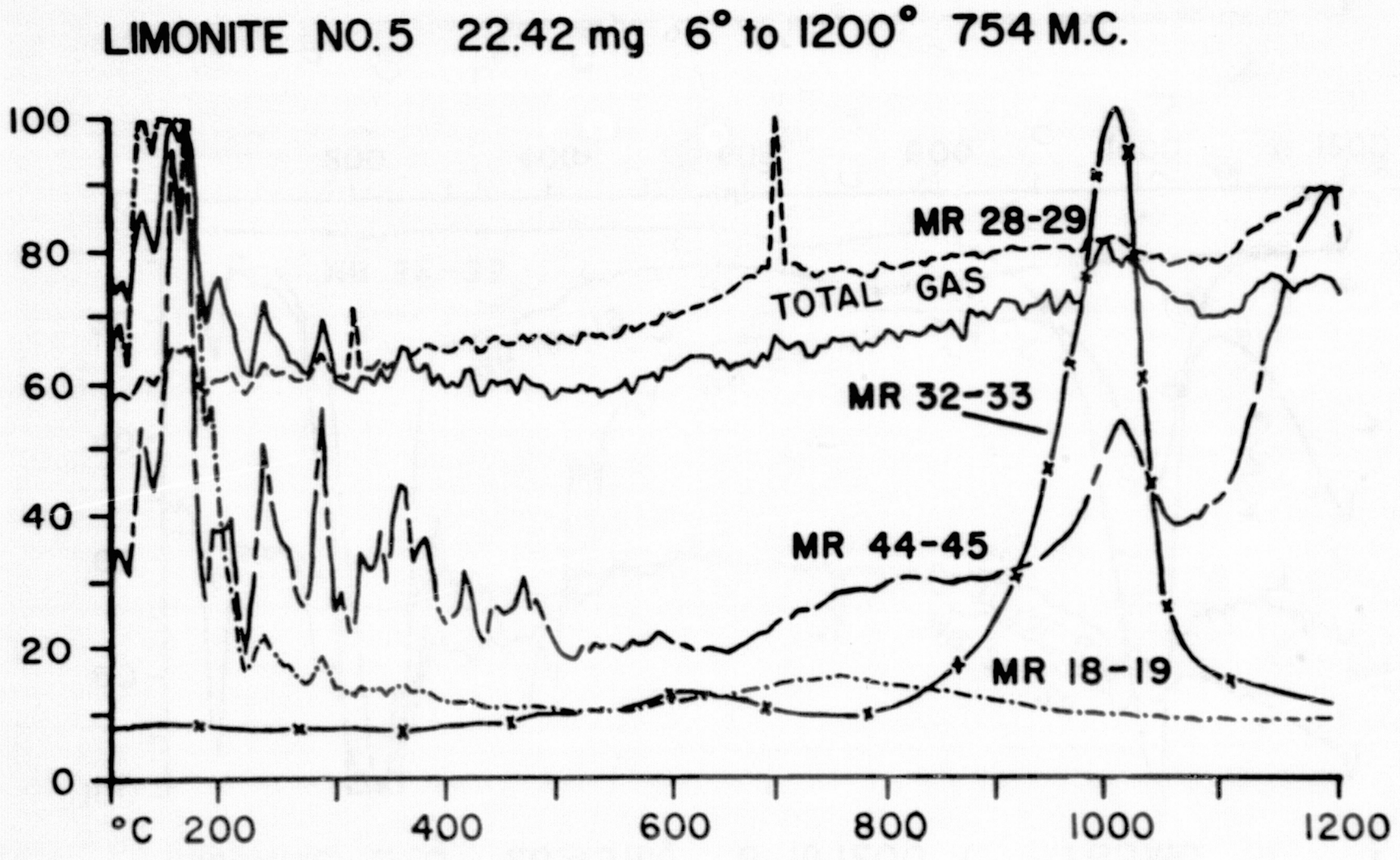


Figure 1. Gas release patterns for natural limonite.

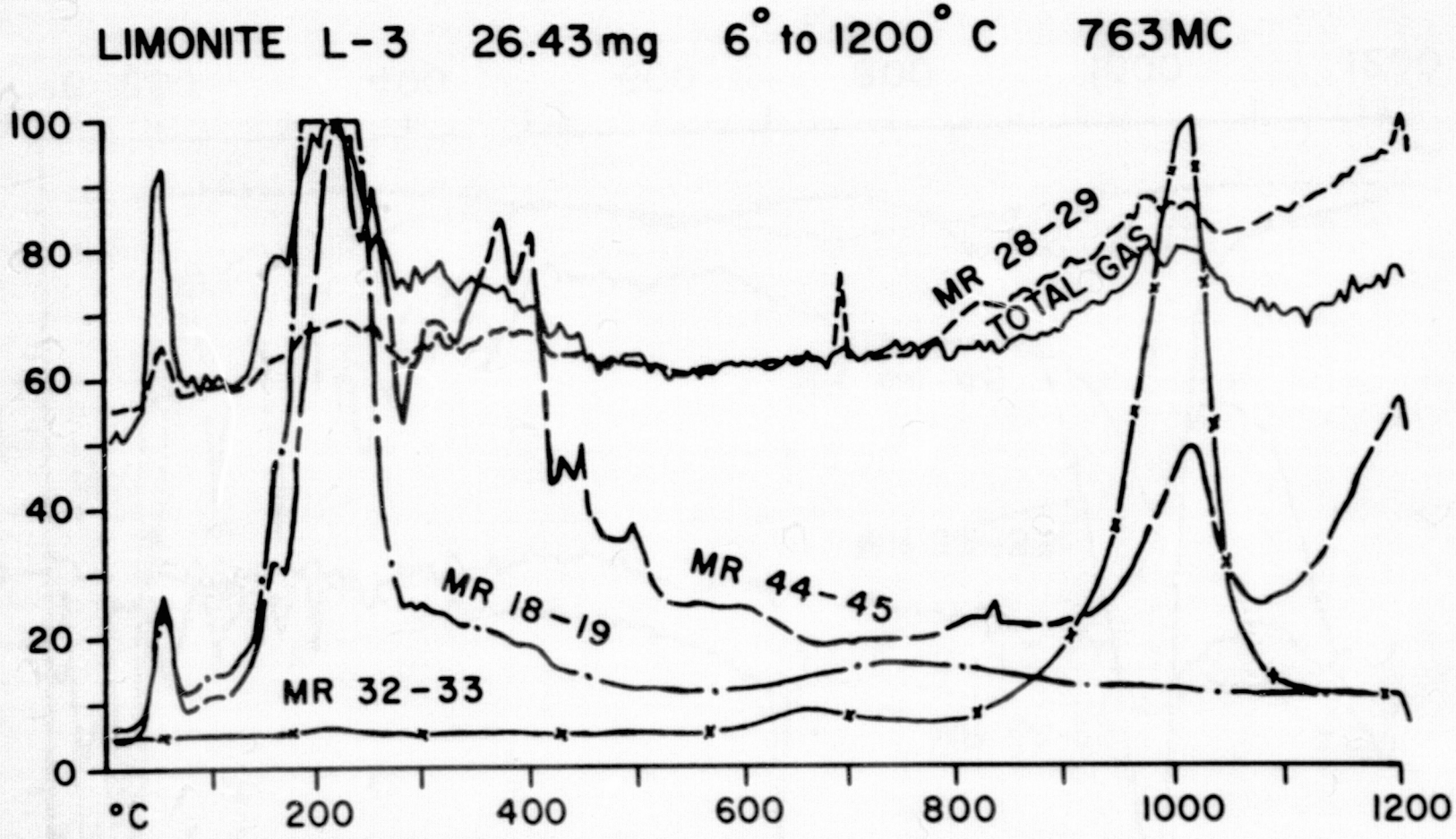


Figure 2. Gas release patterns for limonite heated for 72 hours in vacuum at 150°C.

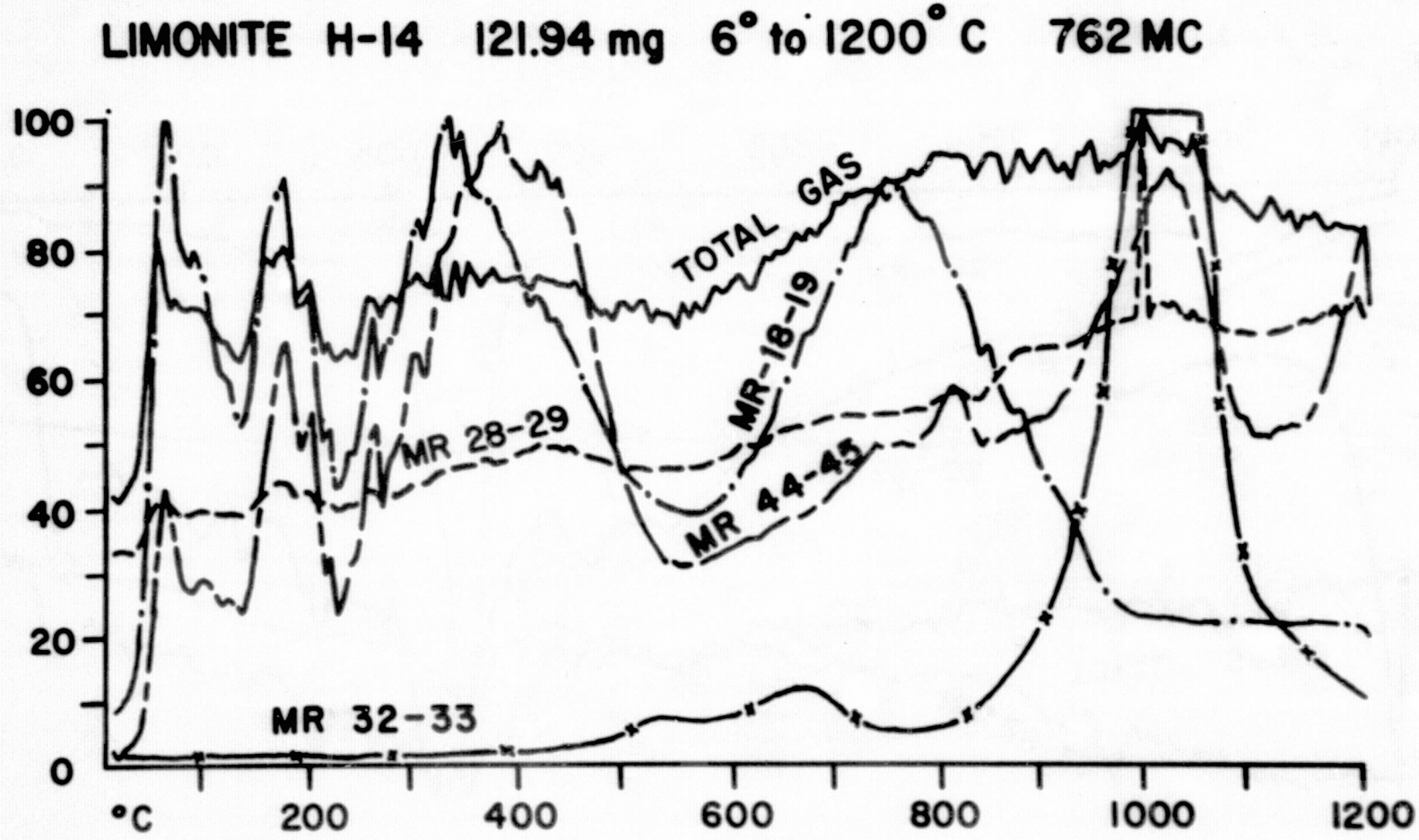


Figure 3. Gas release patterns for limonite heated for 24 hours at 275°C in Helium.

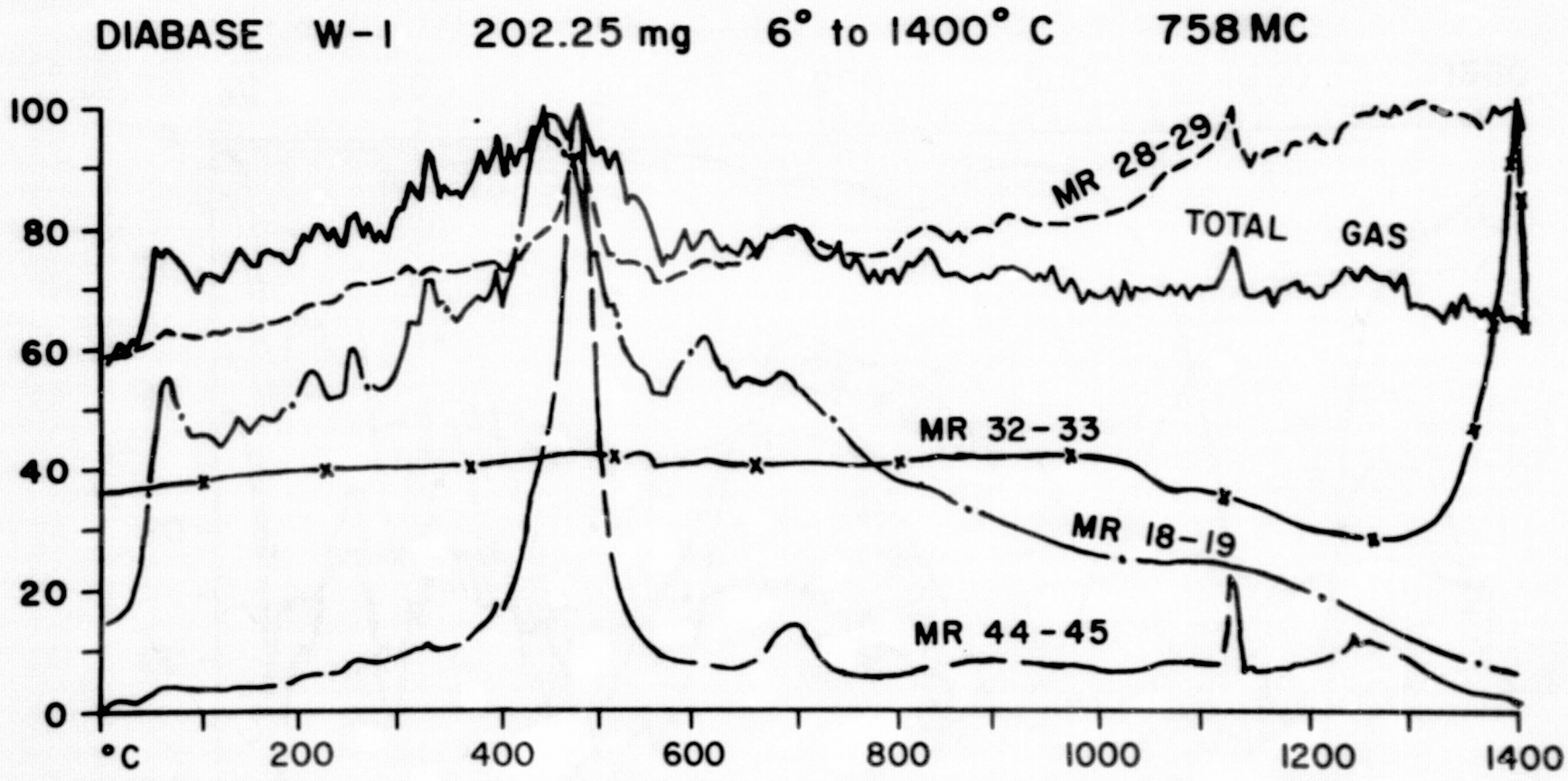


Figure 4. Gas release patterns for natural W-1.

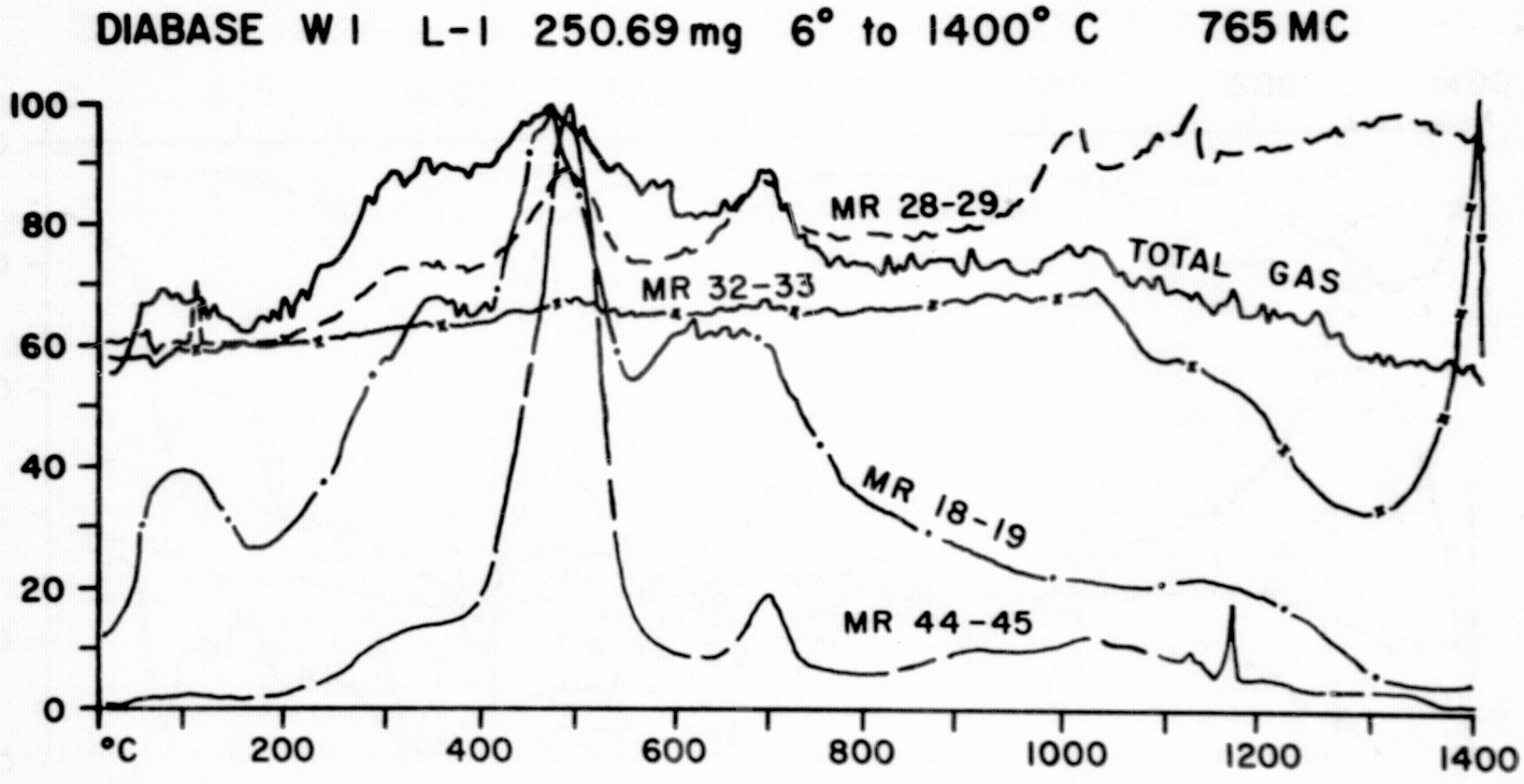


Figure 5. Gas release patterns for W-1 at 150°C for 72 hours in vacuum.

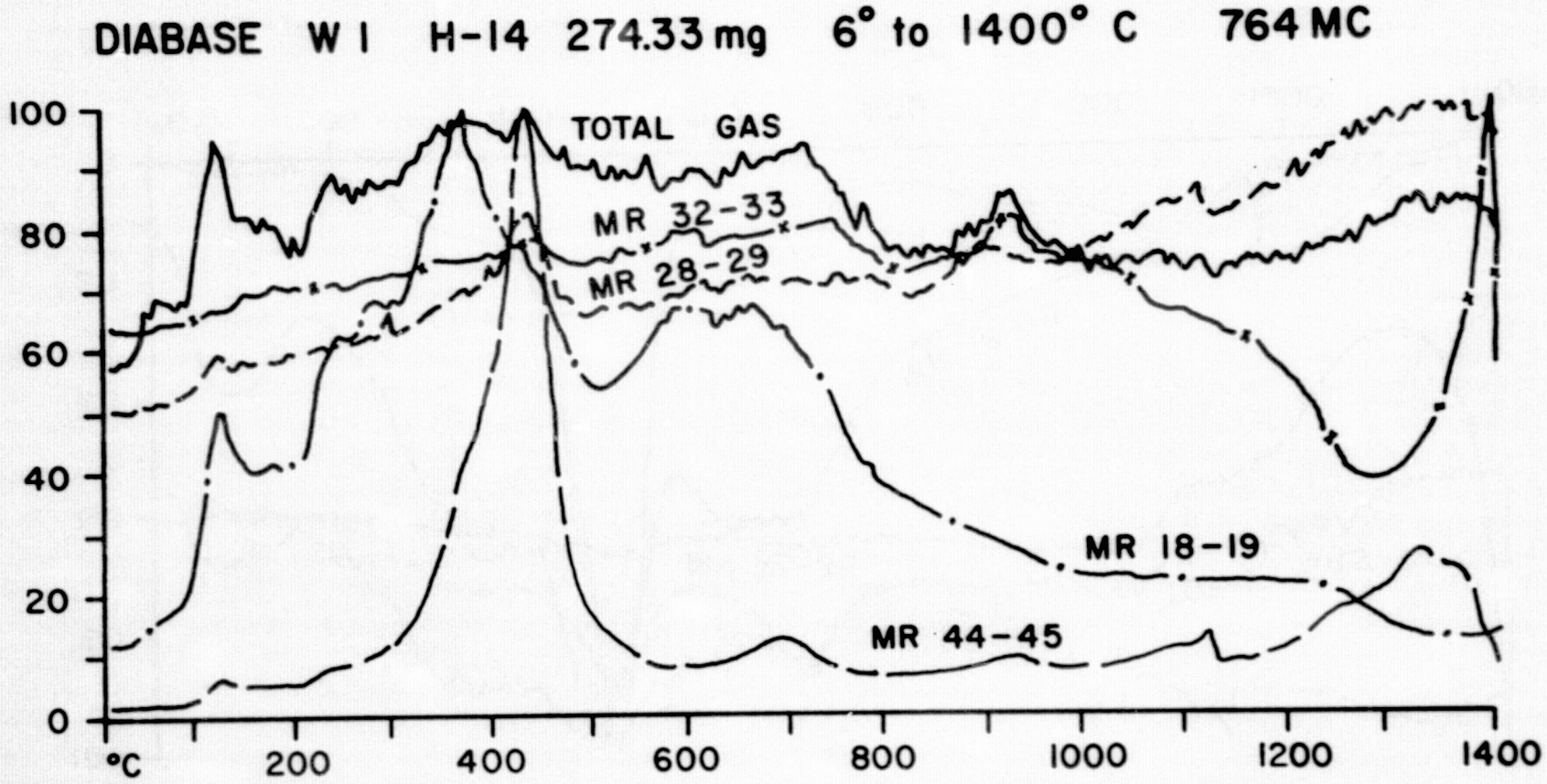


Figure 6. Gas release patterns for W-1 heated for 24 hours at 275°C in Helium.

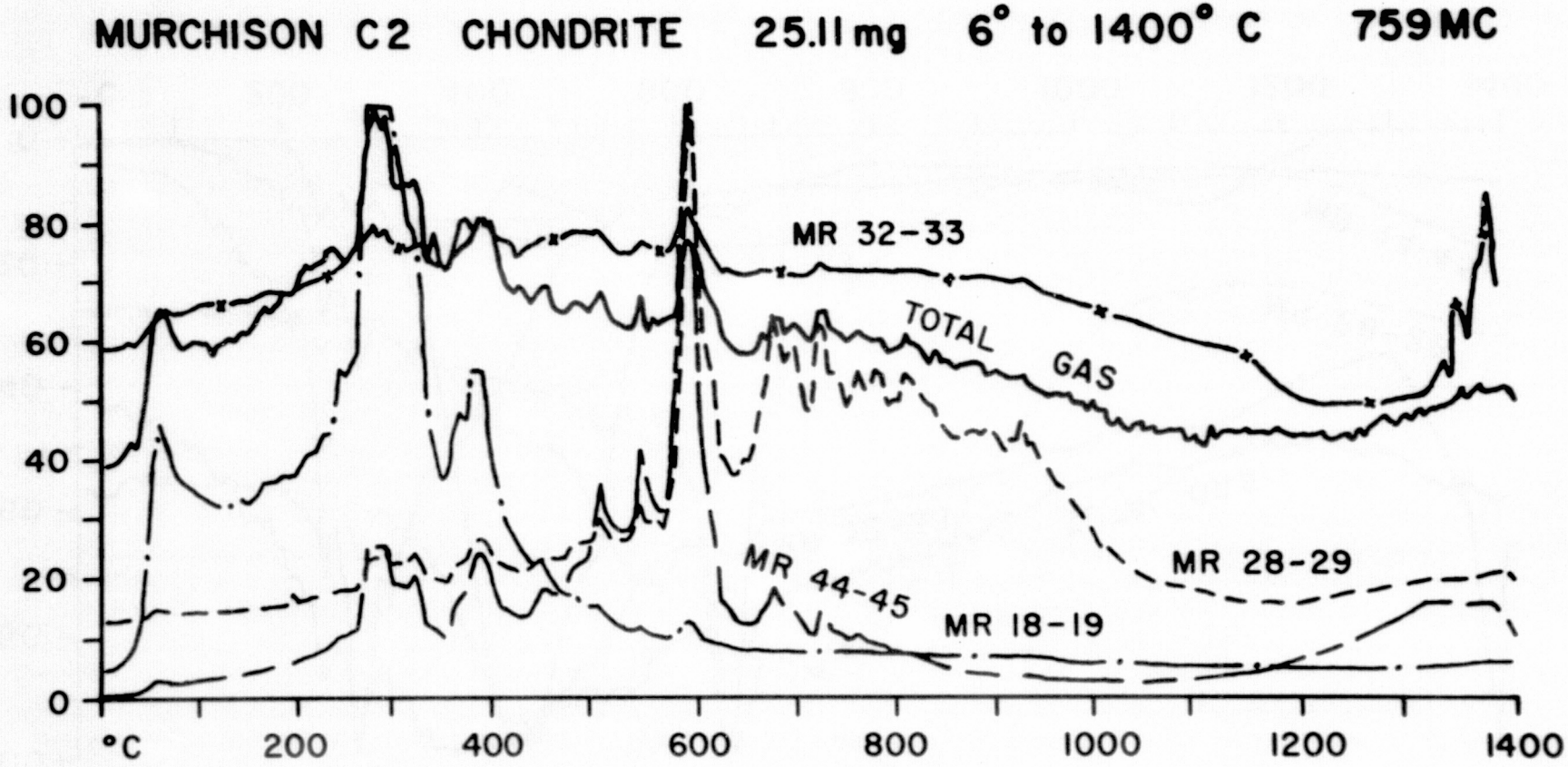


Figure 7. Gas release patterns for natural Murchison sample.

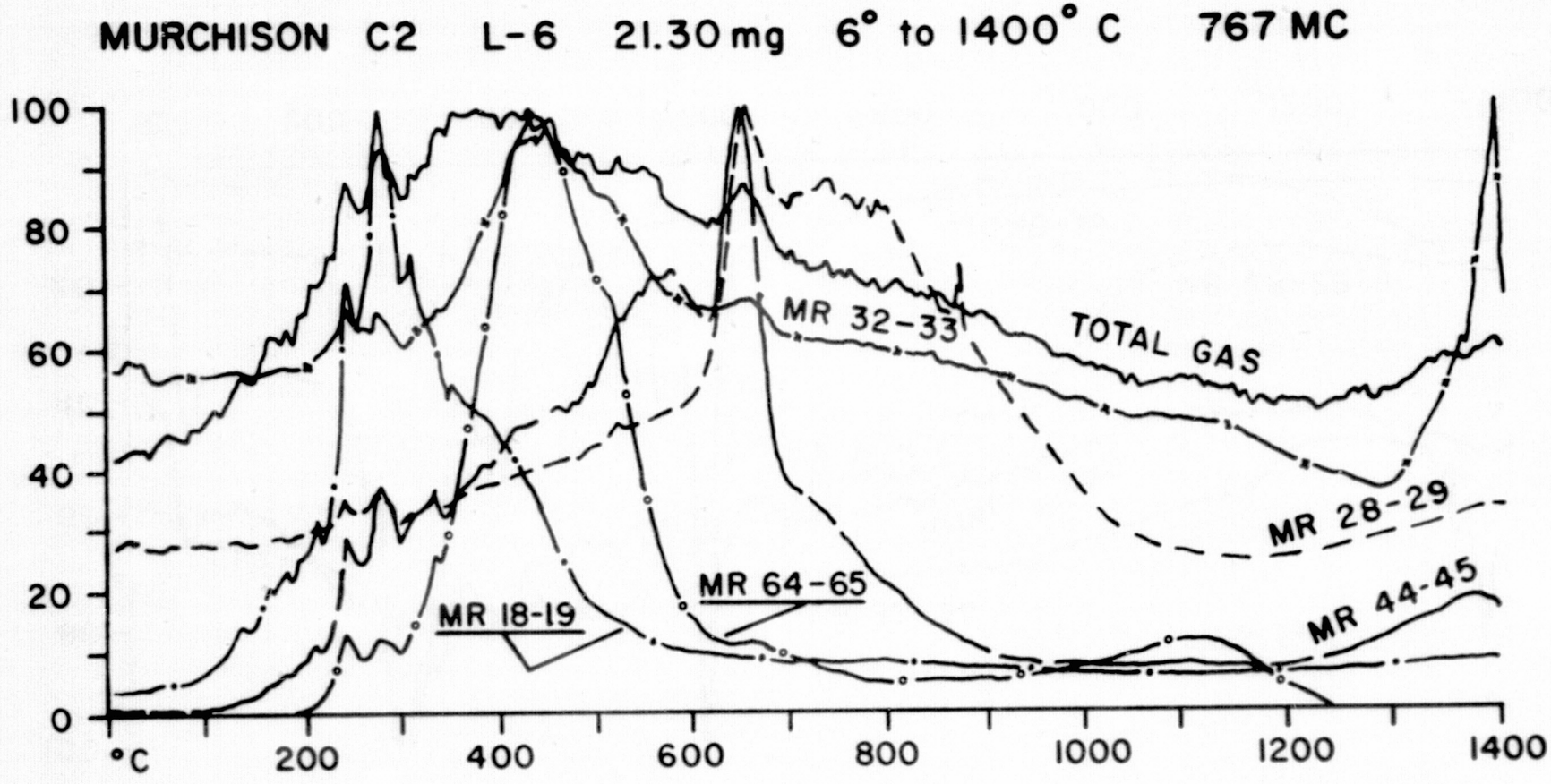


Figure 8. Gas release patterns for Murchison sample heated for 72 hours at 150°C in vacuum.

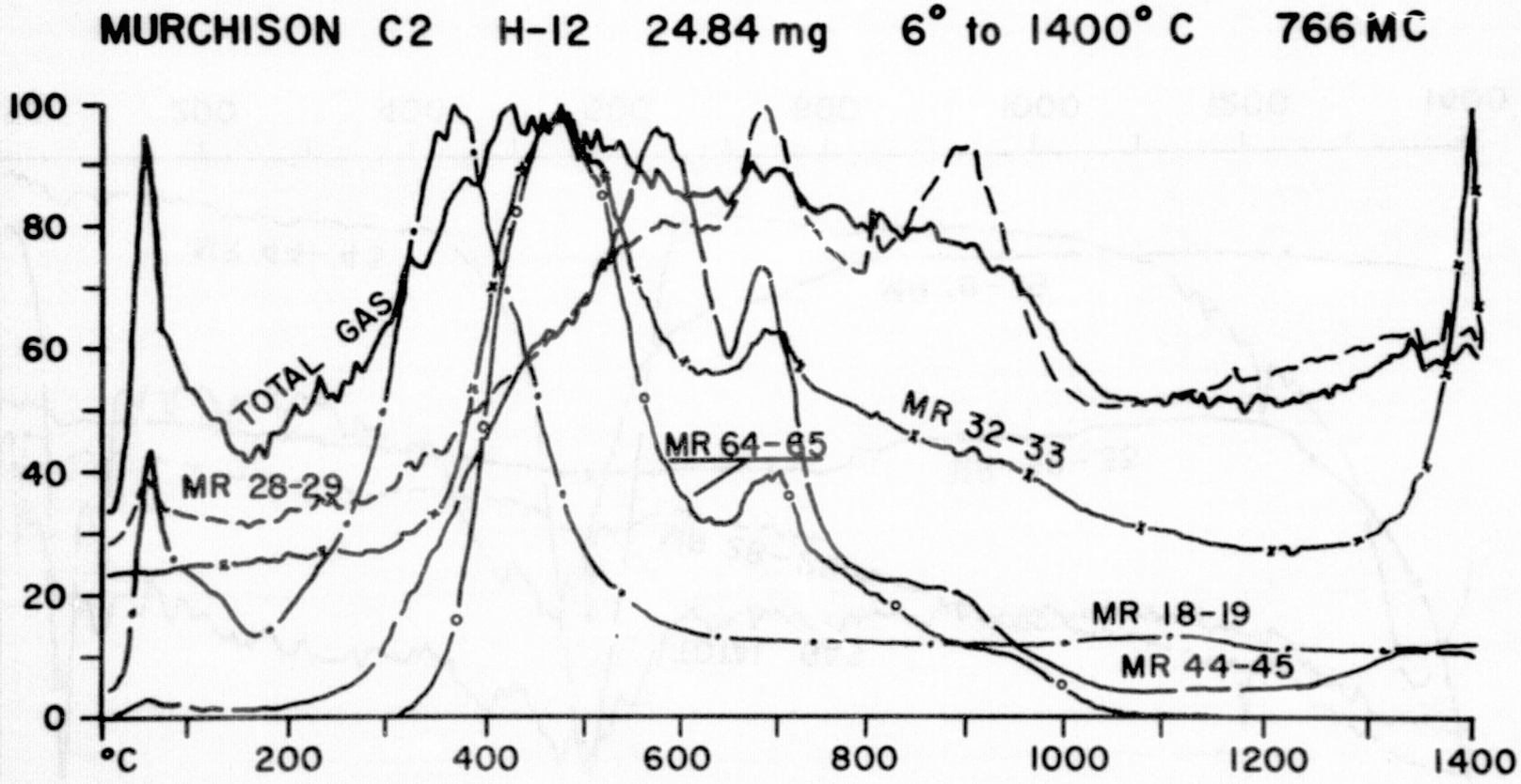


Figure 9. Gas release patterns for Murchison sample heated at 275°C for 24 hours in Helium.

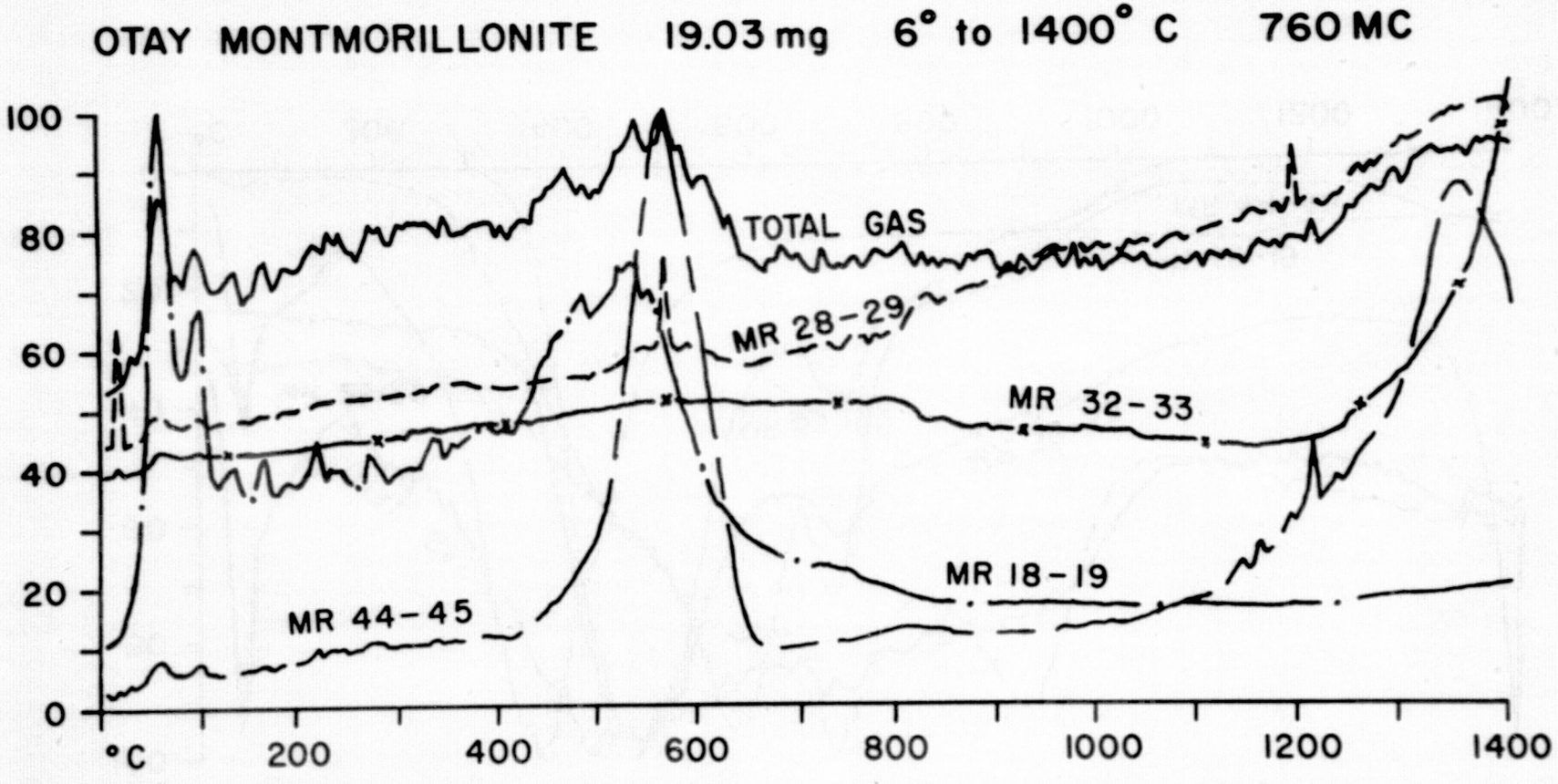


Figure 10. Gas release patterns for natural Otay Montmorillonite sample.

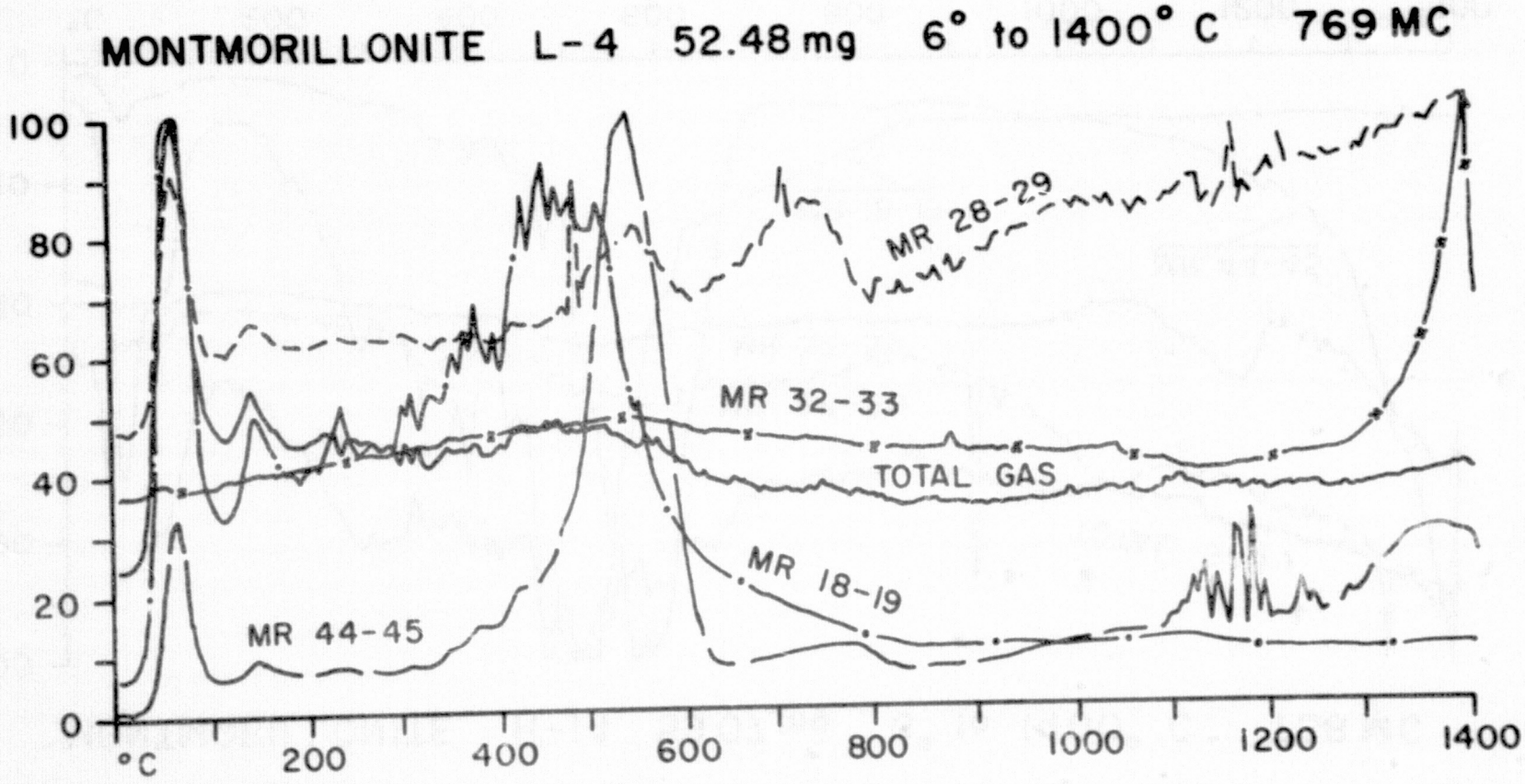


Figure 11. Gas release patterns for Otay Montmorillonite sample heated for 72 hours at 150°C in vacuum.

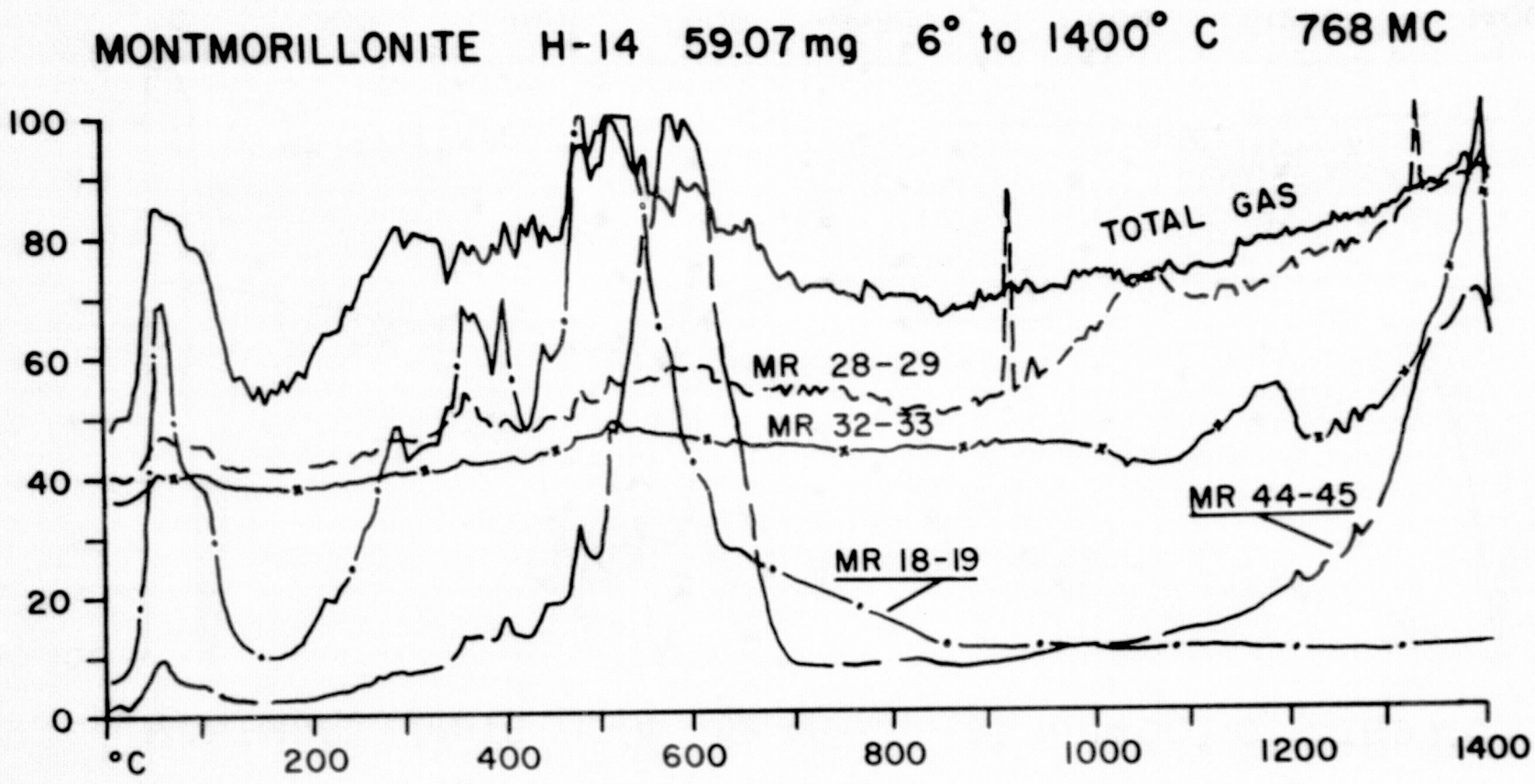


Figure 12. Gas release patterns for Otay Montomorillonite heated for 24 hours at 275°C in Helium.

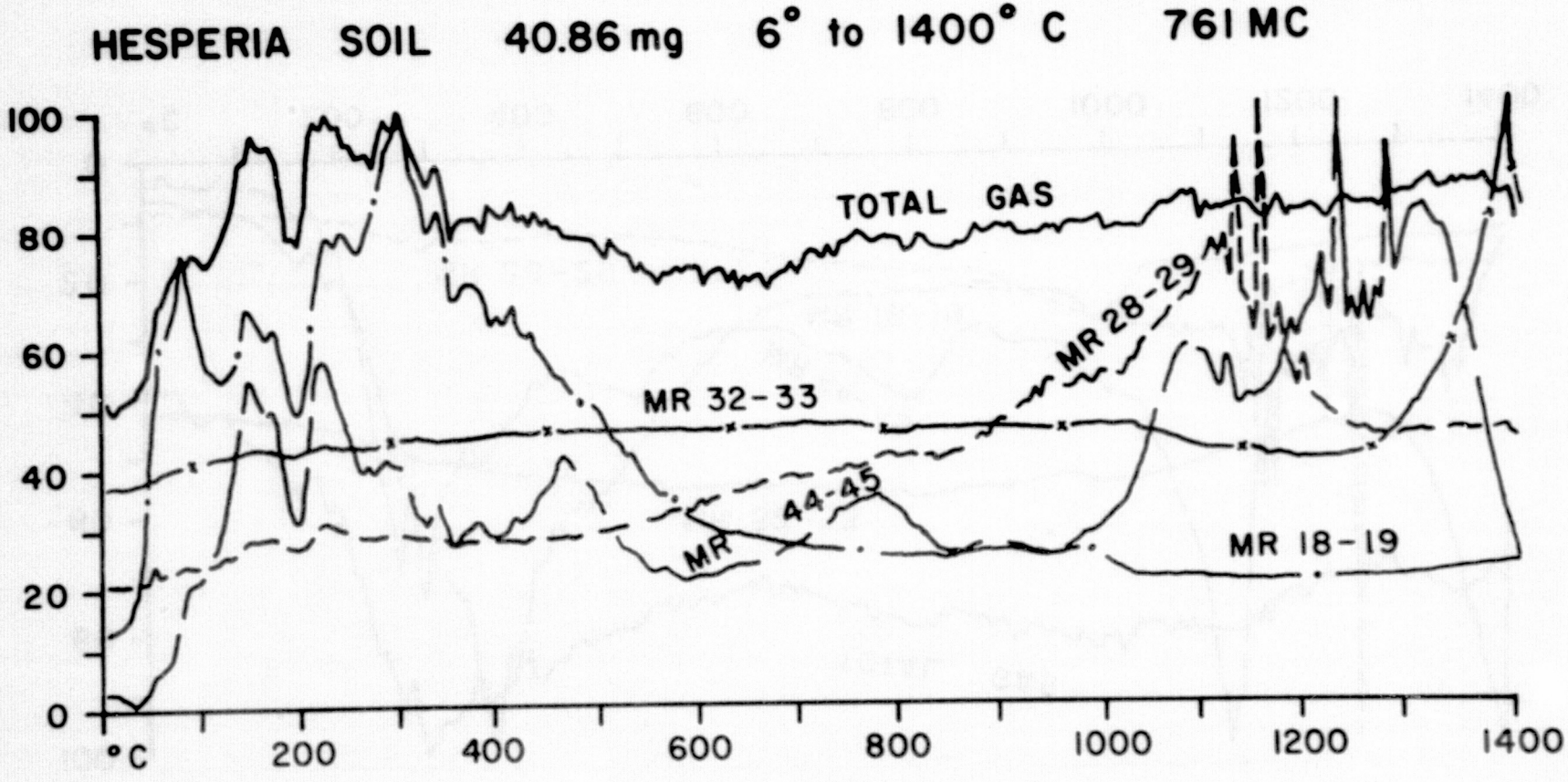


Figure 13. Gas release patterns for natural Hesperia soil sample.

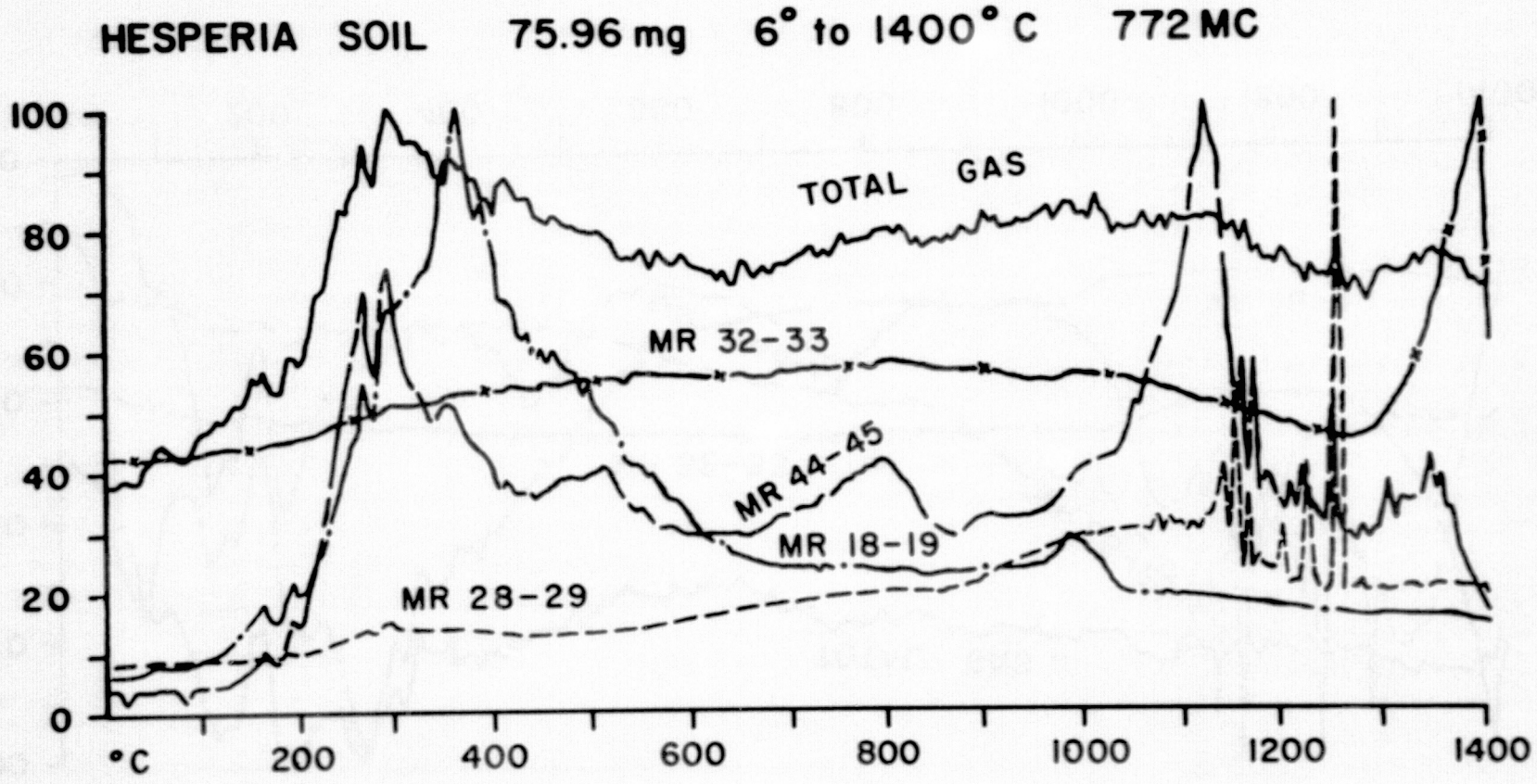


Figure 14. Gas release patterns for Hesperia soil heated for 72 hours at 150°C in vacuum.

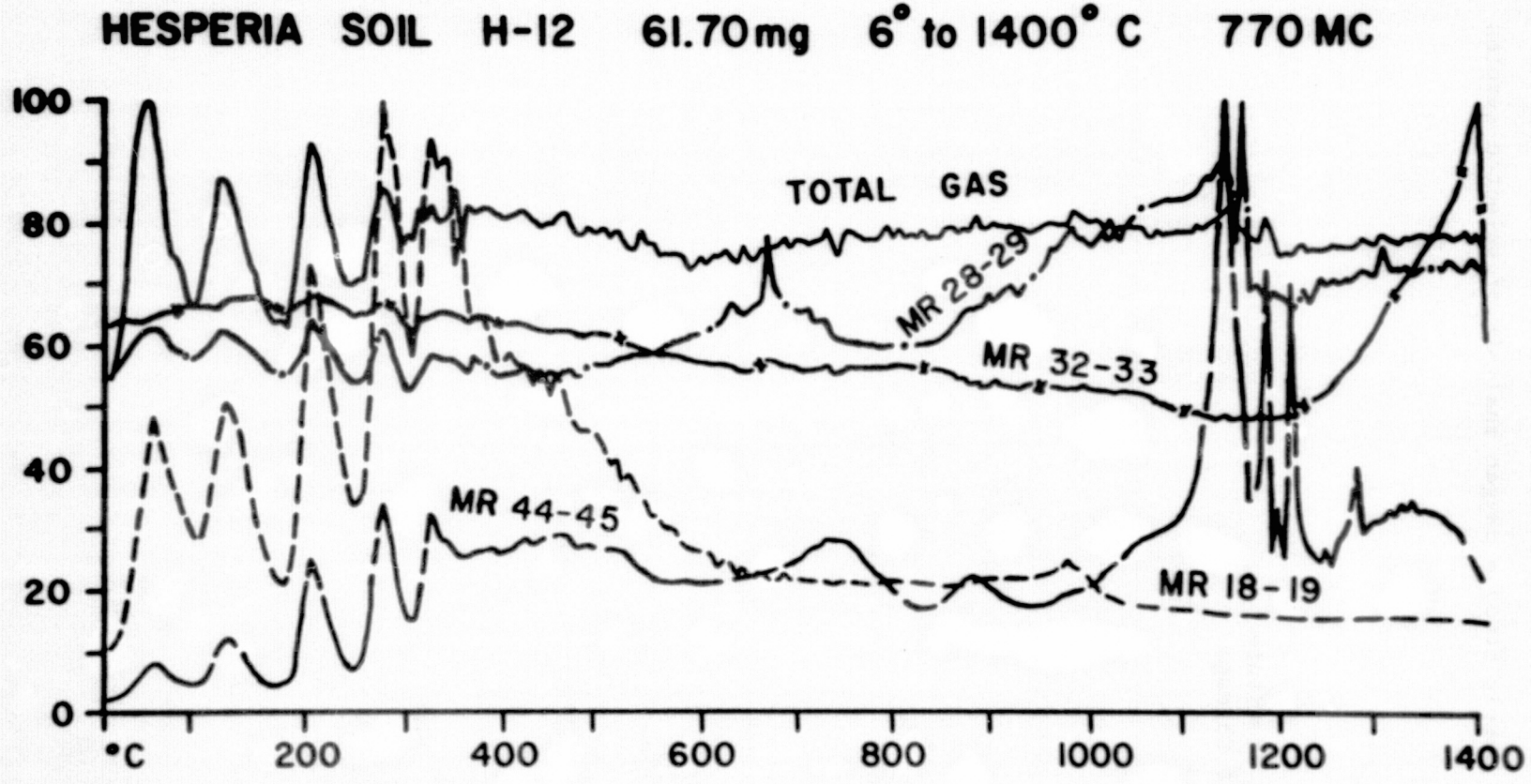


Figure 15. Gas release patterns for Hesperia soil sample heated for 24 hours at 275°C in Helium.

Preliminary Mars Sample Study - oxygen analysis of selected samples

R. N. Clayton

The Enrico Fermi Institute
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March 11, 1974

Dr. Elbert A. King, Jr.
Geology Department
University of Houston
Houston, Texas 77004

Dear Elbert:

We have completed our analyses of the Mars sterilization samples. We analyzed the untreated portions in duplicate to get some idea of our reproducibility on the hydrous samples. They present us with some analytical difficulties, since our procedure requires a vacuum outgassing at ≥ 100°C to remove atmospheric contaminants. You can see that the reproducibility is poorer for Murchison and the Hesperia soil than for the anhydrous diabase.

Sample	O content (wt.%)	δO^{18} (°/oo rel. to SMOW)
W-1, unheated	43.7	6.54
" "	44.0	6.55
W-1, heated	44.9	6.47
Murchison, unheated	33.8	8.16
" "	34.0	7.24
Murchison, heated	36.6	5.07
Limonite, unheated	41.1	8.87
Limonite, heated	36.4	9.77
Montmorillonite, unheated	48.6	16.92
" "	48.1	16.99
Montmorillonite, heated	49.7	16.20
Hesperia soil, unheated	48.0	11.29
" " "	46.7	11.98
Hesperia soil, heated	47.8	10.85

The measured oxygen contents are determined by measuring the O_2 liberated, and are calculated on the basis of the pre-outgassing weight. If water is lost in vacuum at 100°C, the oxygen yield will be low. Presumably this could happen only for the unheated samples. This effect may account for the fact that Murchison and montmorrilonite have higher oxygen contents after heating.

All samples except the diabase have undergone changes in isotopic composition by 1 or 2°/oo (some increasing, some decreasing). It may not be surprising that the change in Murchison is greatest, since it is highly inhomogeneous in isotopic composition, containing phases with at least a 20°/oo spread.

It will be possible to make a much more definitive assessment of these results when you have other chemical and mineralogical information on the changes brought about by heating. I hope we will all be kept informed so that we may amplify the interpretations of the experiments in light of the complete evidence.

Sincerely yours,

Bob

Robert N. Clayton

RNC/mb

Documentation of Selected Samples for Preliminary Mars Sample Studies

I. C. Jones
Department of Geology
University of Houston
Houston, Texas

LIMONITE

Limonite* is usually described as amorphous or cryptocrystalline. Originally limonite had been considered to possess a definite formula, 2 Fe_2O_3 . 3 H_2O, but is now known to consist mainly of one or more cryptocrystalline hydrated iron oxides. Deer, Howie, and Zussman (1962) list a group of 3 limonite analyses, from which the variable nature of the composition is apparent (Table 1).

Table 1. Limonite Analyses

(after Deer, Howie & Zussman, 1962)

	1	2	3
Fe_2O_3	83.59	79.34	73.74
Al_2O_3	-	1.56	6.80
SiO_2	2.93	4.80	2.91
TiO_2	-	-	0.27
FeO	-	-	0.17
CaO	0.81	-	0.04
P_2O_5	-	0.93	-
H_2O	12.67	13.34	14.17
Total	100.00	99.97	100.00

As far back as 1919, Posnjak and Merwin concluded that no series of hydrates of ferric oxide exists and that the only existing hydrate is ferric oxide monohydrate, Fe_2O_3 . H_2O, occurring in 2 polymorphic forms.

*The name limonite comes from the Greek, λειμων meaning "meadow" because of its common occurrance in bogs.

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The crystalline character of "limonites" has been investigated by x-rays by Dasgupta & Maitra (1952). X-ray studies of hydrated iron-oxide minerals show that only two distinct varities occur in nature. These are polymorphs of the monohydrate $Fe_2O_3 \cdot H_2O$ or FeO(OH). The monohydrate, Goethite has a crystal structure orthorhombic space group Pbnm (Goldstaub, 1931) with a = 4.60, b = 10.0 and c = 3.03 Å. Lepidochrocite or γ ferric oxide monohydrate is also orthorhombic, space group Cmcn, with a = 3.06, b = 12.51, and c = 3.87 (Goldstaub, 1931).

The term "limonite" is commonly used by mineralogists to describe the hydrated oxides of iron with poorly developed crystalline character. These are generally composed of goethite with so small a crystal size that the external crystalline characteristics are masked. Adsorption of moisture on the crystallites was earlier interpreted to provide the molecular formula $2\ Fe_2O_3 \cdot 3\ H_2O$. When the limonite is sufficiently finely divided that x-ray diffraction lines are broadened, this is usually the case. A few limonites may consist of lepidochrocite or a mixture of goethite and lepidochrocite. Goethite is produced, according to Weiser (1935), when gels and sols of hydrous basic ferric oxide are aged, while lepidochrocite is obtained during oxidation of ferrous compounds. The color of these monohydrates arise from their respective structures, with goethite pigments being yellow, and lepidochrocite, brown.

These are decomposed upon heating yielding anhydrous ferric oxide, Fe_2O_3. Goethite decomposes in air @ 250°C, and heating for 1 hr @ 300°C in either air or nitrogen will complete decomposition to α ferric oxide, hematite where [100], [010], and [001] in goethite become [001], [010] and [210] in hematite, which has a hexagonal structure (Goldstaub, 1935). Appreciable line broadening may be observed due to the minute size of

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these multi-domain crystals, however this effect is not uniform. Lines such as those resulting from (102), (104), and (214) become very broad, while others such as (110), (113), (116), and (300)are comparatively sharp. This effect is due to the disruption of some planes during dehydration, while others remain in the original state of packing. At higher temperatures greater than 300°C the rebuilding of these disrupted planes is effected, giving the periodicity expected in crystals of hematite, thus sharpening the lines. The same effects causing goethite to yield α ferric oxide upon decomposition act during the heating of lepidochrocite, which, after heating @ 300°C for 1 hour yields γ ferric oxide, maghemite. This change, like the goethite to hematite change, is pseudomorphic in character (Bernal et al, 1957), with the maghemite [001], [140], and [1$\bar{1}$0] axes respectively parallel to the original lepidochrocite directions, [100], [010], and [001].

X-RAY DIFFRACTION DATA*

Goethite			Lepidocrocite			Hematite			Maghemite		
d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	I	hkl	d(Å)	I	hkl
4.98	15	020	6.27	100	020	3.67	35	102	7.91	1	101
4.18	100	110	3.29	60	021	2.69	100	104	6.94	2	102
3.38	10	120	2.473	30	130	2.514	75	110	5.90	6	110
2.69	30	130	2.362	15	111	2.204	25	113	5.33	1	112
2.58	8	021	2.086	12	131	2.072	3	202	4.82	6	113
2.520	3	101	1.935	30	150;002	1.838	30	204	4.29	2	114
2.490	15	040	1.848	10	022	1.692	45	116	3.73	6	210
2.452	25	111	1.733	15	151	1.635	2	121	3.40	7	213
2.252	10	121	1.567	8	080	1.597	15	108	3.20	3	214
2.192	20	140	1.532	7	200	1.484	20	214	2.95	30	220
2.009	2	131	1.523	15	132	1.452	25	300	2.78	3	300
1.920	6	041	1.493	2	220	1.346	6	208	2.638	4	310
1.799	7	211	1.452	2	081	1.310	10	1,0,10	2.514	100	313
1.770	2	141	1.436	7	171			119	2.408	2	226
1.721	20	221	1.417	1	062	1.257	8	220	2.315	2	320
1.694	10	240	1.391	3	221	1.226	3	306	2.230	2	323
1.661	4	060	1.369	8	152	1.211	3	223	2.086	15	400
1.606	6	231	1.264	1	203	1.187	6	312	1.865	1	420
1.564	15	160;151	1.218	2	082			218	1.820	3	423
1.509	10	250	1.201	2	202	1.162	6	2,0,10	1.701	9	426
1.467	4	320	1.193	2		1.138	7	314	1.670	2	430
1.453	10	061				1.102	8	226	1.604	20	513
1.418	2	112				1.053	9	2,1,10	1.550	2	520
1.392	7	330							1.525	3	523
1.357	7	311							1.474	40	440
1.317	7	321							1.318	6	620
1.264	2	331							1.272	8	539
1.241	1	142							1.258	3	626
1.198	2	341							1.204	5	4,4,12
									1.115	6	646
									1.086	10	733
									1.043	7	800
									0.983	5	826
									0.963	8	753
									0.932	4	840

(after Rooksby, 1961)

*Intensities are normalized to 100 for the stringest line; intensities above 10 have been rounded off to the nearest multiple of five.

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In the early 1950's an investigation was undertaken to determine the precision and accuracy in chemical, spectrochemical, and modal analyses of silicate rocks. (H. W. Fairbairn, et al., 1951). Instead of preparing synthetic standards for these tests it was decided by the M.I.T. group to prepare standard samples of a natural rock and run replicate chemical analyses on these standards. The diabase standard has been reduced to hand specimens, thin sections, and powdered rock. One thousand-three hundred-eighty-two jars, each containing about 70 grams of this powder, have been labeled W-1. In his discussion of the preparation of the samples, Fairbairn (1951) points out that the matter of contamination of this powder is of no significance with respect to the sample's use as a standard, but in using results of analyses as a measure of the rock's original composition this contamination should be taken into consideration. Alumina, silica, and iron have possibly been introduced into the powder in appreciable amounts as a result of abrasion of the rolls and containers during preparation of the samples.

The aid of various types of laboratories was enlisted with the help of the Office of Naval Research, resulting in over 30 analyses by 24 laboratories within a year.

Chemical Analyses

(Schlecht & Stevens, 1951)

Table 1 contains results of analyses and calculated CIPW norms of the diabase sample (W-1) reported by the 30 collaborating chemists in the study.

Procedures in Chemical Analyses

Silica (SiO_2) - The sample is fused with calcium carbonate, the product then dissolved in acid (usually HCl) and evaporated to dryness, leaving most of the silica dehydrated and insoluble. The portion of SiO_2 remaining in soluble form is recovered by a second dehydration, any remainder being recovered by dissolving the R_2O_3 group and dehydrating with sulfuric acid. Perchloric and sulfuric acids are sometimes used for second or third dehydrations. After collecting the silica, the analyst ignites it at sufficiently high temperatures to provide complete dryness for weighing. The silica is then volatilized with hydrofluoric acid. The crucible and residue are weighed, and the weight of SiO_2 is obtained by difference.

Negative errors result from failure to remove all the silica from the container, especially troublesome when using porcelain vessels, and generally outweigh the positive errors. The positive errors generally result from failure to drive off all water prior to weighing but may result from removal of the glaze of the collecting vessel.

Alumina (Al_2O_3) - The alumina in table one was generally calculated by subtracting from the R_2O_3 group - elements precipitated by neutralizing the acid solution with NH_4CH - the Fe_2O_3, TiO_2, and P_2O_5.

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Table 1

(after Schlecht and Stevens, 1951)

Results of analyses and calculated CIPW norms of diabase sample (W–1), reported by 30 collaborators

[Reports of collaborators are designated by numbers (1–5, 7–24, 26–28, 31–34) in boxheads]

	1	2	3	4	5	7	8	9	10	11	12	13	14	15	16
SiO_2	52.56	52.58	52.12	53.01	52.59	52.59	52.48	52.38	52.45	51.71	52.35	52.42	52.55	51.28	51.28
Al_2O_3	13.91	14.91	15.07	15.09	14.99	15.13	15.19	15.34	15.66	14.86	15.37	15.35	13.70	14.57	16.32
Fe_2O_3	2.28	1.38	1.44	.92	1.06	1.35	1.73	1.35	3.46	4.00	1.31	1.31	2.64	2.60	.28
FeO	8.92	8.78	8.81	9.16	8.89	8.78	8.42	8.66	6.90	7.14	8.67	8.69	8.16	8.28	9.38
MgO	6.67	6.70	6.74	5.69	6.54	6.64	6.52	6.60	6.52	6.69	6.59	6.60	6.68	6.18	6.67
MnO	.17	.16	.16	.13	.21	.16	.10	.11	.18	.16	.17	.17	.18	.53	.12
CaO	10.82	11.00	11.04	10.86	10.88	10.98	10.55	11.19	11.04	10.79	10.95	10.95	10.89	11.42	11.29
Na_2O	2.09	2.14	2.09	2.40	2.28	2.15	2.17	1.98	1.88	2.15	2.01	2.09	2.28	2.48	2.06
K_2O	.74	.68	.60	.66	.69	.71	.61	.60	.65	.82	.62	.68	1.17	.82	1.30
H_2O-	.12	.18	.13	.15	.20	.18		.07	.02	.24	.17	.17	.05	.18	.32
H_2O+	.52	.44	.46	.41	.39	.48	.67	.77	.62	.20	.49	.47	.52	.71	.06
TiO_2	1.12	1.00	1.02	1.01	1.00	1.01	1.04	1.06	.91	1.12	1.08	1.09	1.18	1.41	1.15
P_2O_5	.13	.18	.14	.17	.13	.13	.24	.12	.11	.18	.13	.13	.14	.10	0 (?)
S	.04						0							0	
CO_2							0								
BaO	.06						.04								
SrO					.02		.09								
Li_2O					.03		.02								
Cr_2O_3							.03								
V_2O_3															
Total	[1]100.11	100.13	99.82	99.66	99.92	100.30	99.90	100.22	100.40	100.06	99.92	100.12	100.14	100.04	100.23
CIPW norms															
Quartz	4.74	3.60	4.56	3.72	2.88	3.84	4.20	4.02	6.66	4.50	4.02	3.60	2.82	1.32	
Orthoclase	3.89	3.84	3.34	3.89	4.45	3.89	3.34	3.34	3.89	5.00	3.34	3.89	7.23	5.00	7.78
Albite	17.82	18.34	16.77	20.44	18.86	18.34	18.34	16.77	16.24	17.82	16.77	17.82	19.39	20.96	17.82
Anorthite	26.41	28.91	30.58	28.36	28.63	29.47	30.02	31.14	32.25	28.36	31.41	30.30	23.35	26.13	31.14
Diopside	21.64	20.96	19.16	20.69	20.10	20.37	18.46	19.97	17.30	19.99	18.80	18.95	24.51	24.39	20.62
Hypersthene	19.15	19.98	20.84	18.47	20.50	19.52	19.65	19.68	16.24	15.35	20.68	20.64	16.07	15.30	15.06
Olivine															4.97
Magnetite	3.25	2.09	2.09	1.39	1.62	2.09	2.55	2.09	5.10	5.80	1.86	1.86	3.71	3.02	.46
Ilmenite	2.13	1.98	1.98	1.98	1.98	1.98	1.98	2.13	1.67	2.13	2.13	2.13	2.28	2.74	2.13
Apatite	.34	.34	.34	.34	.34	.34	.34	.34	.34	.67	.34	.34	.34	.34	
Water	.64	.44	.59	.56	.59	.66	.67	.84	.64	.44	.66	.62	.56	.89	.38
Total	100.01	100.55	100.25	99.84	99.95	100.50	99.55	100.32	100.33	100.06	100.01	100.15	100.26	100.09	100.36
Classification:															
Class, Order	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5
Rang, Subrang	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4

Table 1
(continued)

	[1] 17	[1] 18	[1] 19	[1] 20	21	22	23	[1] 24	26	[1] 27	28	[1] 31	[1] 32	33	[2] 34
SiO_2	52.31	52.66	52.61	52.32	52.43	52.21	52.42	52.45	52.09	52.28	52.49	52.20	52.51	52.22	52.25
Al_2O_3	15.18	14.96	14.66	15.41	14.86	16.56	15.04	14.83	18.57	14.92	14.51	14.50	15.28	15.19	15.13
Fe_2O_3	1.74	1.08	1.32	1.22	1.57	4.26	1.43	1.13	1.33	3.86	1.19	1.45	1.51	1.92	1.02
FeO	8.55	9.22	8.80	9.12	8.67	6.80	8.80	8.95	8.81	7.02	8.98	9.10	8.57	8.45	9.07
MgO	6.79	7.09	6.66	6.76	6.70	5.49	7.09	6.75	4.67	6.61	6.69	6.57	6.66	6.60	6.74
MnO	.18	.26	.17	.12	.17	.21	.18	.20	.23	.22	.20	.16	.13	.18	.17
CaO	11.15	10.70	10.88	10.88	10.91	11.12	11.06	10.86	10.64	10.92	10.90	11.02	10.81	11.07	10.96
Na_2O	2.20	1.91	1.96	2.02	2.62	1.61	1.94	1.78	1.98	1.98	2.18	1.78	2.09	1.82	2.11
K_2O	.60	.41	.84	.64	.67	.66	.62	.64	.75	.58	.66	.57	.54	.74	.60
H_2O-	.16	.13	.23	.03	.16	.09	.18	.08	.23	.18	.16	.10	.04	(3)	.16
H_2O+	.50	.58	.46	.61	.56	1.17	.62	[4] 1.04	.67	.48	.72	1.16	.38	.54	.46
TiO_2	1.13	.94	1.14	1.03	1.13	.53	1.11	1.09	.10	1.00	1.21	1.37	1.28	.95	1.03
P_2O_5	.15	.08	.16	.12	.11	.08	.13	.10	.15	.16	.17	.18	.06	.09	.22
S					.03								.00		
CO_2		0													
BaO					.02								[5] .03		
SrO													[5] .001		
Li_2O													[5] .02		
Cr_2O_3					.02								[5] .01		
V_2O_3													[5] .07		
Total	100.64	100.02	99.89	100.28	[6] 100.62	100.79	100.62	99.90	100.22	100.21	100.06	100.16	[7] 100.01	99.77	99.94
CIPW norms															
Quartz	3.36	4.68	3.96	3.66	1.50	8.82	4.14	5.22	3.96	6.90	3.54	5.64	4.62	5.10	3.36
Orthoclase	3.34	2.22	5.00	3.34	3.89	3.89	3.34	3.34	4.45	3.34	3.89	3.34	2.78	3.89	3.34
Albite	18.34	16.24	16.77	16.77	22.01	13.62	16.24	15.20	16.77	16.77	18.34	15.20	17.82	15.20	17.82
Anorthite	30.02	30.86	28.63	31.41	26.97	36.14	30.58	30.58	39.48	30.02	27.80	29.75	30.86	31.41	30.02
Diopside	20.03	17.59	20.31	18.27	21.64	14.68	19.13	18.46	10.51	18.88	21.02	19.52	17.99	18.66	21.93
Hypersthene	19.85	24.09	20.31	22.16	18.85	14.88	21.77	21.96	21.81	15.68	20.21	20.21	20.54	20.01	18.77
Olivine	2.55	1.62	1.86	1.86	2.32	6.26	2.09	1.62	1.86	5.57	1.86	2.09	2.09	2.78	1.39
Magnetite	2.13	1.67	2.13	1.98	2.13	1.06	2.13	2.13	.15	1.98	2.28	2.74	2.43	1.82	1.98
Ilmenite	.34	.34	.34	.34	.34	.34	.34	.34	.34	.34	.34	.34	.34	.34	.67
Apatite	.67	.71	.70	.64	.72	1.26	.80	1.12	.90	.66	.88	1.27	.42	.54	.62
Water															
Total	100.63	100.02	100.01	100.43	100.35	100.95	100.56	99.97	100.23	100.14	100.16	100.10	99.89	99.75	99.90
Classification:															
Class, Order	III, 5	III, 5	III, 5	III, 5	III, 5	II, 4	III, 5	III, 5	II, 5	III, 5	III, 5	III, 5	III, 5	III, 5	III, 5
Rang, subrang	4, 4	4, 3	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4	4, 4

[1] Mean of 2 analyses. [2] Corrected for sulfur (−0.02). [3] Received too late for inclusion in calculation in chap. 3. [4] Dried at 100° C. [5] Loss on ignition. [6] Spectrographic determinations. [7] Corrected for sulfur (−0.01). [8] Also reported PbO, 0.002, and NiO, 0.001 (spectrographic determinations).

Total iron (Fe) - Iron in solution is first either reduced to the ferrous state and then titrated to the ferric state, or else the ferric iron is titrated with titanous ion.

Ferrous oxide (FeO) - The sample is dissolved in a mixture of H_2SO_4 and HF in a large crucible with a tight-fitting lid. This crucible is then placed in a beaker of dilute sulfuric acid, and usually boric acid, and the solution is titrated with an oxidizing agent such as $KMnO_4$ in an atmosphere of steam or CO_2.

Calcium Oxide (CaO) - Calcium oxalate is precipitated from the filtrate of the R_2O_3 separation and ignited to the oxide.

Magnesium Oxide (MgO) - Magnesium is precipitated as magnesium ammonium phosphate and weighed as the pyrophosphate ($Mg_2P_2O_7$).

Sodium Oxide (Na_2O) - The sample is decomposed using the J. Lawrence Smith procedure: sintering with a mixture of $CaCO_3$ and NH_4Cl. Substitution by some of $BaCl_2$ for NH_4Cl in the sinter mixture allows greater ease in sintering and removes the sulfate. Four analysts decomposed the samples with HF and H_2SO_4 giving a more complete recovery of alkalis. The mixed chlorides of potassium and sodium are weighed and the potassium is then separated and weighed, giving sodium by difference.

Potassium oxide (K_2O) - Decomposition procedures are similar to Na_2O, determined in the same portion of sample used for K_2O determination. In determination, the potassium is weighed as K_2PtCl_6, $KClO_4$, or potassium cobaltinitrite. As in sodium oxide, a flame photometer may also be used.

Phosphorous pentoxide (P_2O_5) - Phosphate is separated from a nitric acid solution by precipitation as ammonium phospho-molybdate, and can be weighed in this or another form.

Further discussion on the comparison of reliability of the various methods of analysis for different chemical constituents can be found in the paper by Schlecht & Stevens (1951).

Figure 1 is a group of histograms based on the chemical data in Table 1.

Histograms Based on Results in Table I
(after Schlecht and Stevens, 1951)

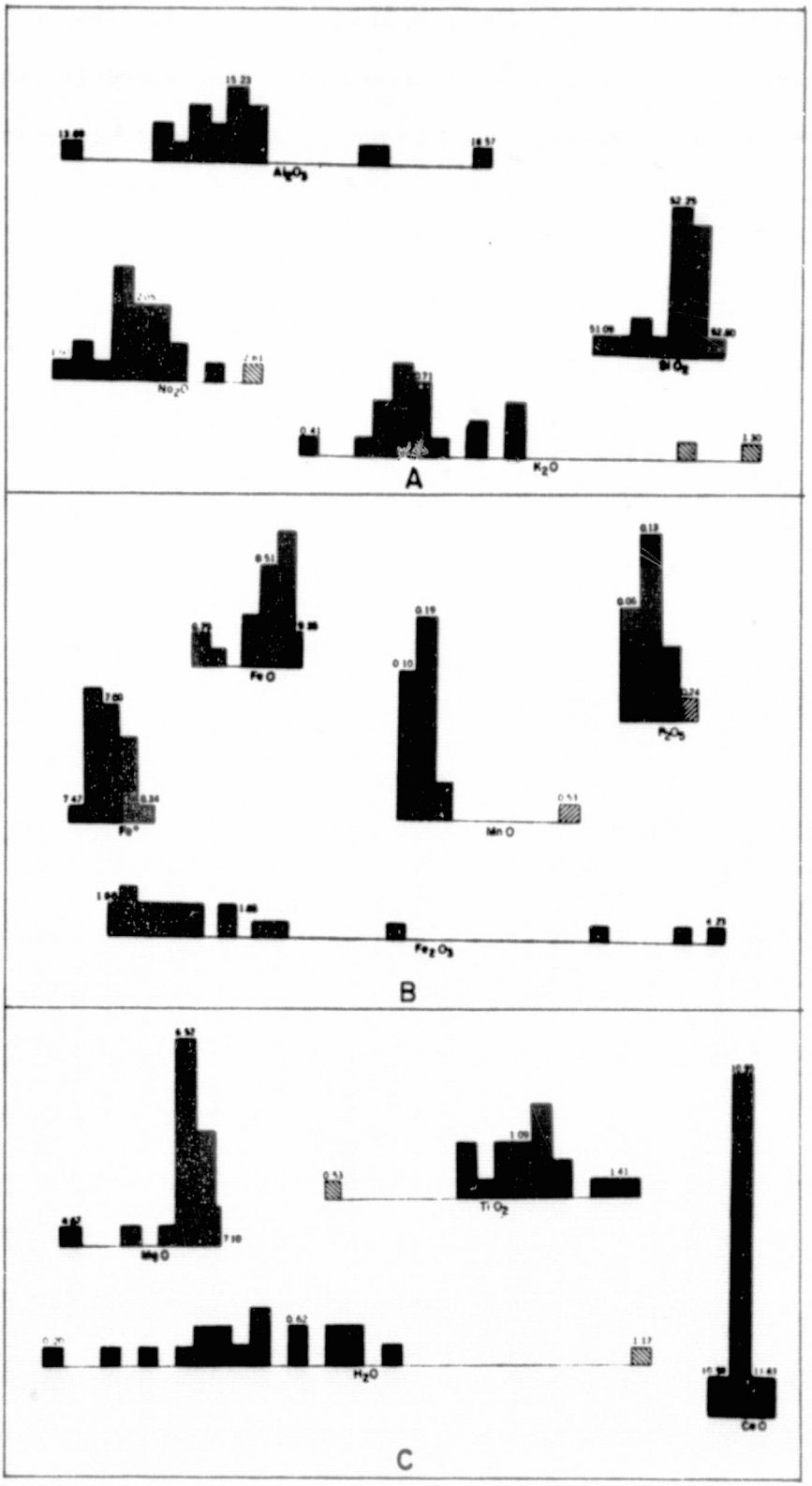


Figure I

Spectrochemical Analysis

(Ahrens & Fairbairn, 1951)

To determine Ca, Al, Mg, Mn, and Fe, strontium was used as the internal standard following the procedure of Kvalheim (1947).

Results of spectrochemical analyses for major elements can be found in Table 2a. Results of analyses for some rarer elements can be found in Table 2-b.

Table 2a. Precision of determinations in rock analyses by 24 laboratories[1]

[Computations: $\bar{x}$, arithmetic mean; s, standard deviation; $s_{\bar{x}}$, standard error; E, relative error]

	Diabase (W-1)			
	$\bar{x}$	S	$S_{\bar{x}}$	E
SiO_2	52.25	0.41	0.09	0.167
TiO_2	1.09	1.79	.04	3.59
Al_2O_3	15.23	.938	.20	1.31
Fe_2O_3	1.85	.953	.21	11.24
FeO	8.51	.707	.15	1.77
Fe°	7.88	.180	.04	.50
MnO	.19	.086	.02	9.47
MgO	6.52	.520	.11	1.70
CaO	10.95	.197	.04	.38
Na_2O	2.05	.230	.05	2.39
K_2O	.71	.196	.04	5.89
H_2O+	.62	.245	.05	8.42
P_2O_3	.13	.0414	.01	6.93

1. Analyses recalculated to 100 percent, omitting H_2O-.
2. Fe° indicates total Fe as metallic iron. Percent not included in summation.

(After Ahrens and Fairbairn, 1951).

Table 2b - Comparison of spectographic and chemical methods of analysis for rarer elements in the granite and diabase samples (After Ahrens, 1951).

Diabase Standard

Constituents	Spectrographic			Chemical	
	1	2	3	4 Field test)	5 (Laboratory test)
BaO	0.028	0.043	0.030	---	---
BeO	0	0	---	---	---
B_2O_3	---	.003	---	---	---
CoO	.0044	.0032	.0038	0.002	0.0052
Cr_2O_3	.018	.019	.016	---	---
CuO	.016	.011	.0055	.01	.016
Ga_2O_3	.002	.0016	.0026	---	---
La_2O_3	.0038	0	0	---	---
Li_2O	.002	---	.002	---	---
MoO	0	0	---	.0007	---
Nd_2O_3	---	---	0	---	---
NiO	.006	.01	---	.02	.010
PbO	0	0	.00078	.0006	.0006
Rb_2O	.0016	---	[1] .007	---	---
Sc_2O_3	.0023	.0052	[2] .0078	---	---
SrO	.05	.017	.030	---	---
V_2O_3	.032	.032	.050	---	---
Y_2O_3	0	---	0	---	---
ZnO	---	---	---	---	.011
ZrO_2	.0068	.013	.013	---	---
MnO	---	.18	.20	---	---

1. Rubidium analyses determined in three different ways.
2. A value of 0.00055 percent Sc_2O_3 is given by A. Kvalheim.

Modal Analyses

(Felix Chayes, 1951)

The diabase (W-1) was found to consist of augite and plagioclase (labradorite) with smaller amounts of quartz, potash feldspar, biotite, and opaque minerals. Quartz is generally associated with potash feldspar in micropegmatic intergrowths. The opaque minerals are mostly or all oxides. Neither sulfides nor olivine was detected in this fine grained sample. These sections were prepared from 12 chips of the diabase. The slides were then etched with hydrofluoric acid and stained with sodium cobaltinitrite. A continuous 500 mm area was outlined on each slide and a point-counter analysis was run with a horizontal intercept distance of 0.3 mm with a 1.0 mm interval between traverses.

Table 3 gives results of modal analysis of W-1 converted to percent by weight. The means and standard deviations are listed in Table 4. The following specific gravity factors have been applied to the volume percentages: Quartz, 2.66; potash feldspar, 2.56; plagioclase, 2.71; pyroxenes, 3.30; biotite- 312; opaque minerals, 5.2; nonopaque accessory minerals, 3.2.

The 1972 values for USGS-W-1 are listed in a paper on international geochemical reference samples by F. J. Flanagan (1973), and are listed in Table 5.

Table 3 - Diabase modes converted to percent by weight

Slide No.	Quartz	Potash feldspar	Plagio-clase	Pyroxene	Biotite	Accessories	
						Opaque	Non-opaque
1	0.8	2.3	46.8	45.9	1.4	2.6	0.1
2	1.7	2.7	45.7	45.0	1.4	3.1	.3
3	1.6	2.5	45.6	45.9	.9	3.5	.0
4	2.0	2.6	46.4	44.4	2.0	2.6	.1
5	1.8	3.7	43.6	44.9	1.8	4.0	.2
6	2.7	3.3	40.9	48.6	1.1	3.1	.2
7	2.7	3.4	44.6	44.0	2.0	3.1	.2
8	1.7	4.2	43.6	43.9	2.0	4.5	.1
9	1.3	1.8	48.3	43.0	2.7	2.8	.1
10.	1.5	2.5	46.8	41.0	2.3	3.0	.0
11.	1.9	3.6	44.2	44.2	1.9	3.3	.4
12.	2.0	3.0	43.1	46.0	2.1	3.6	.1
Average .	1.8	3.0	45.0	45.0	1.8	3.3	.2

(After Chayes, 1951)

Table 4 - Average modes for test rocks.

Mineral	Diabase (12 sections)	
	Mean	Standard dev.
Quartz	1.8	0.5
Potash feldspar	3.0	.7
Plagioclase	45.3	2.0
Pyroxene	45.0	1.5
Biotite	1.8	.5
Muscovite	---	---
Opaque accessories	3.3	.6
Nonopaque accessories	.2	---
Average length of count . . .		1345

(After Chayes, 1951)

Table 5:
U.S.G.S. - W-1

		Trace Elements	
SiO_2	52.64	Ag ppm	0.081
Al_2O_3	15.00	As ppm	1.9
Fe_2O_3	1.40	Au ppb	3.7
FeO	8.72	B ppm	15
MgO	6.62	Ba ppm	160
CaO	10.96	Be ppm	0.8
Na_2O	2.15	Bi ppm	0.046
K_2O	0.64	Br ppm	0.4
H_2O+	0.53	C ppm	-
H_2O-	0.16		
TiO_2	1.07		
P_2O_5	0.14		
MnO	0.17		
CO_2	0.06		
Sum	100.26		
Total Fe as Fe_2O_3	11.09		

(After Flanagan, 1973)

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OTAY MONTMORILLONITE

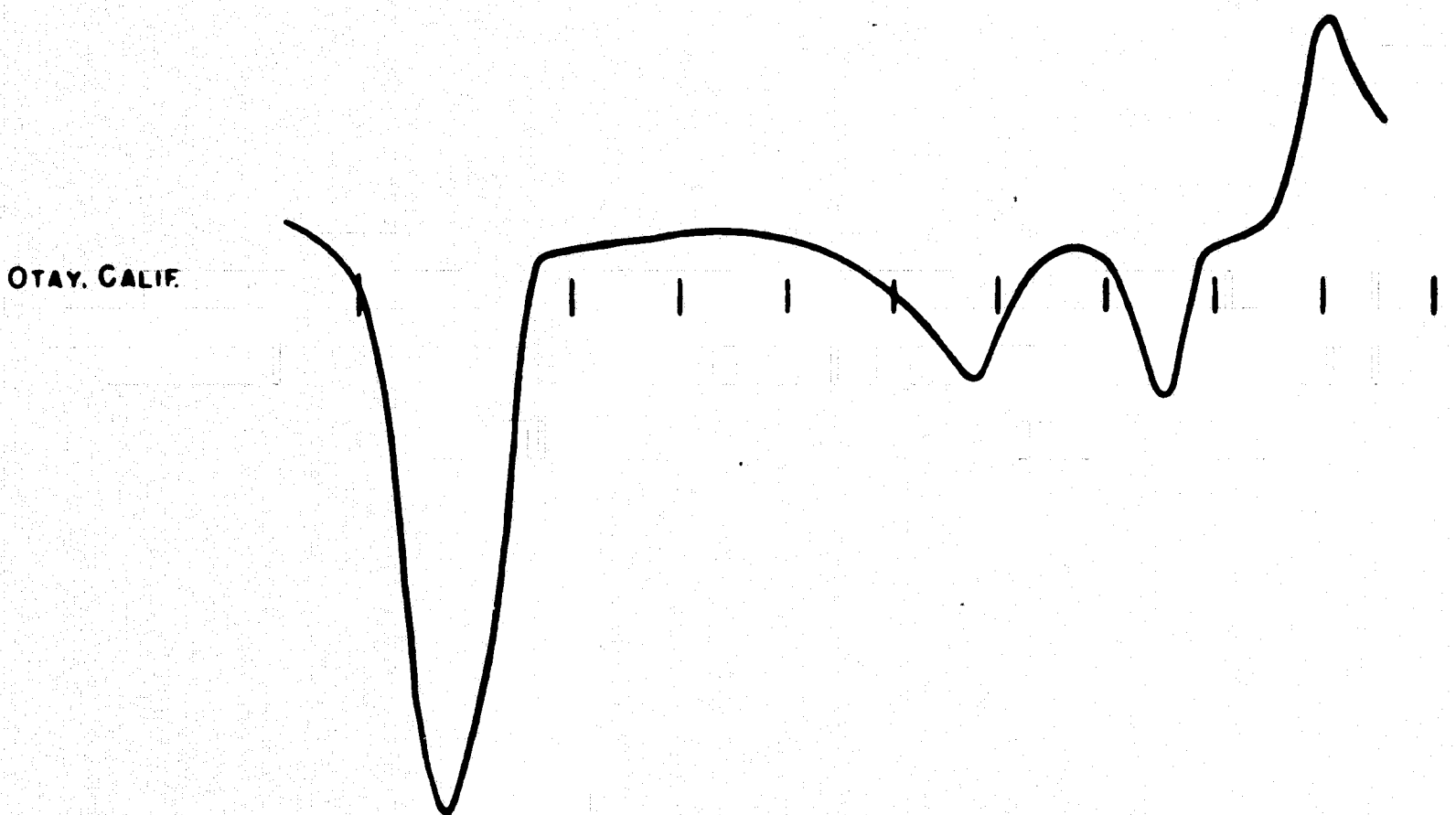
Montmorillonite from Otay, California represented one of the samples in the Montmorillonite group selected for the clay minerals standards project (American Petroleum Institute Research Project (American Petroleum Institute Research Project 49). One hundred pounds of waxy white material was collected from a bentonite clay pit 3 miles east of Otay, California. This bentonite is thought to be in the same horizon as the Pliocene ash beds just south of Tijuana, Mexico (Kerr and Kulp, 1949).

As a preliminary study, differential thermal analyses of the reference clay mineral specimens were performed (Kerr et al., 1949). Clay minerals are known to undergo several exothermic or endothermic changes as do most hydrous minerals. Dehydration or decomposition is an example of an endothermic change. The Otay clay is a high grade montmorillonite with sodium and calcium as interlayer ions. The formula for the Clay Montmorillonite is:

$$(Al_{1.43}Fe_{.03}Mg_{.64})\ (Al_{.01}Si_{3.99})\ O_{10}(CH)_2(Na_{.12}\ Ca/_{2.07})$$

The thermal curves obtained (Figure 1) show no indication of thermally active impurities. Of the two high temperature peaks, one occurs at 690°C and the other at 1000°C. The temperature maximum of the first peak depends on particle size, perfection of layer stacking, gross substitution, and the fraction of the substituted atoms in critical position. The second endothermic peak results from breakdown of the montmorillonite structure. This temperature is affected by substitution in both the octahedral and tetrahedral positions. Aluminum-silicon substitution and magnesium-aluminum substitution are the most significant temperature determining factors. The exothermic peak is related to the magnesium content of the octahedral

Figure-1
(after Kerr et al. 1949)



DIFFERENT THERMAL ANALYSIS
OF MONTMORILLONITE

layer, so that high magnesium and low iron content result in a considerably higher peak temperature, while low iron content broadens this peak (Table 1).

Table 1

Octahedral Position			Tetrahedral Position	Inter-	Characteristic Peak Temperatures		
Al	Mg	Fe	Al	layer	1st Endo.	2nd Endo.	Exo
1.43	.64	.03	.01	.19	670	850	1010

The indices of refraction of the Otay sample were found to be α = 1.491, β = 1.495, and γ = 1.495. Microscopic examination revealed 1-2% Sericite, 1% quartz, 1/2 - 1% orthoclase, and traces of limonite and ferromagnesian minerals as impurities present in the sample. (Kerr et al., 1949).

Chemical analysis of one specimen of Otay montmorillonite revealed the following composition (Kerr et al., 1950): $(Al_{1.43}\ Fe_{.03}\ Mg_{.64})\ (Al_{.01}\ Si_{3.99})\ O_{10}\ (OH)_2\ (Na_{.12}\ Ca/_{2.07})$, with the number of ions in octahedral coordination calculated as 2.10 (Table 2).

Table 2. Results of Chemical Analysis

SiO_2	52.52%
Al_2O_3	16.10
Fe_2O_3	0.51
FeO	0.26
MgO	5.69
CaO	0.47
Na_2O	0.82
K_2O	0.23
H_2O+	8.16

Table 2 (Continued)

H_2O-	14.68
TiO_2	0.16
MnO	0.003
C	Trace
Total	99.603

(After Kerr et al. 1950)

The pH value for the Otay sample was determined (Kerr et al., 1950):

pH of Water	Sample Readings	Average pH
6.54	7.55 7.54 7.54 7.53	7.54

Spectrographic analysis of the Otay montmorillonite (Wheeler et al., 1950) revealed:

	Al%	Ba%	Be%	B	Ca%	Cr%	Co%	Cu%	Ga%	Fe%	Pb%
P*	5	.04	.0005	.005	.6			.007	.007	.5	.05
S**		.04	?	.007		.0007	.001	.0005	.006		.02

	Li%	Mg%	Mn%	Mo%	Ni%	K	Si	Ag	Na
P	Trace	3.1	.004			Present	Major		.3
S	.09		.005	.003	.001			.0001	

	Sr	Ti	V	Zn	Zr
P	.01	.02	.007		.008
S	.03		.006	.03	.05

*Phillips Research Lab Determination

**Shell Oil Co. Determination

It was noted that the Otay montmorillonite has a significantly lower aluminum, iron, and calcium content than other montmorillonite, while the magnesium content is high.

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MURCHISON METEORITE

The largest known fall of a type II carbonaceous chondrite occurred in the desert 85 miles north of Melbourne, Australia, on September 28, 1969. In addition to an initial description, details of the fall can be found in a paper by Lovering et al. (1971). A short description was published by Ehmann et al. (1970), and in 1971, E. Jarosewich reported a chemical analysis of the Murchison meteorite. A more recent description and inorganic analysis of this meteorite can be found in a publication of the Smithsonian Institution by Fuchs et al. (1973), from which this summary draws heavily. Recent analyses of the organic constituents have been published in papers by Levy et al. (1973) and James A. Lawless (1973).

The Murchison meteorite has a higher proportion of inclusions (including chondrules) to matrix than do most other type II carbonaceous chondrites. In overall appearance it is most similar to the Murray C2 meteorite.

As other C2 meteorites, Murchison consists of two main parts - a black matrix and various types of inclusions. Fuchs et al. (1973) have divided the non-matrix portion of this meteorite into four distinct types:

(1) Single crystals and crystal fragments

(2) White inclusions

(3) True chondrules

(4) Xenolithic fragments

The type one inclusions range from a few microns to millimeter size. They are divided into two main subtypes (a) fragmental pieces and single crystals of individual minerals contained directly within the black matrix and (b) individual mineral phases that appear to have grown within the

matrix. The crystals and crystal fragments consist of euhedral and angular olivines, angular pyroxenes, angular chromites, and angular glass fragments. Calcite, gypsum, magnetite, and two poorly characterized soft, dull beige phases appear to have grown within the matrix.

Most of the olivine is homogeneous, but a small percentage is moderately to strongly zoned. There is at least twice as much olivine as pyroxene. Olivines associated with grains of metal show an absence of fayalitic compositions.

Zonal variations in fragments of zoned olivines were found to range from 5 - 40 mole percent Fa, in some cases being not a normal concentric zoning, but rather changing from one Mg-rich edge to an opposite Fe-rich edge, and in rare cases reverse zoning could be observed.

The type two inclusions generally are white, but a few tend to be blue or dark green. They range from approximately 0.5 to 4.5 millimeters in diameter, and tend to be rounded to elliptical in shape. Unlike true chondrules, these inclusions cannot be removed from the matrix as a unit. Many possess crenulated edges which extend into the matrix on a fine scale. Most of these inclusions are forsterite with the sugary texture common to olivine. A few of the white inclusions consist not of olivine, but of spinel with calcite or spinel with clinopyroxene. Accessory spinel, calcite, diopside, troilite, pentlandite, whewellite, and chromite are also noted as intergranular phases.

Some of the inclusions consist of white forsterite interspersed with flakes of a spinach green mixture of polymorphs of chamosite $\pm$ serpentine.

The blue patches consist mainly of hibonite, perovskite, and spinel.

The true chondrules, type three inclusions are not very abundant in the Murchison meteorite. They range in color from white to black, and in size generally from 0.05 - 0.8 millimeters, the few white spheres, however, being 0.1 millimeters or smaller.

These white chondrules consist of fine grained shreds of either clino- or orthoenstatite with minor olivine and calcite rarely present.

The black spheres generally contain granular aggregates of subhedral to anhedral olivine surrounded by streaks of glass or the dark green layer silicate. Small patches of the soft beige phase occur in some chondrules. One chondrule contained olivine with composition Fa 58-59 in a matrix of pigeonitic pyroxene (Fs50), but in general, the olivine is nearly pure forsterite.

Metal is present in most of the chondrules as specks, with some as big as 50-150 microns. These individual grains are uniform in composition but grain to grain variation averages from 4.5 - 5.7% Ni, with one metal grain consisting of 9.6% Ni and patches of high Ca-Al-silicate glass also are present.

The fourth type of inclusion is xenolithic fragments, six fragments of a C3 chondrite ranging from a few to 13 millimeters, and one fragment of an unknown meteorite type (1.2 mm). This xenolith consists of blocky, jointed pieces of pure forsterite in a glass matrix with traces of troilite, metal, and euhedral chromite.

The C3 type fragments contain sulfides in abundance (7 vol. %), and an almost complete absence of metal. The composition of the olivine shows a peak at 5-10 mole % Fa. The composition of the pyroxenes ranges from Fs 2-8 to Fs 15-22.

TABLE 1a (wt. %).—Comparison of chemical analyses Murchison meteorite
(after Fuchs et al., 1973)

	This Work	Data of Jarosewich (197)
Fe^0	0.03	0.13
Cu	0.015	n. d. (6)
NiO	1.73	1.75
CoO	0.076	0.08
FeS	(1)	7.24
SiO_2	27.22	29.07
TiO_2	0.099	0.13
Al_2O_3	2.05	2.15
Cr_2O_3	0.402	0.48
FeO	(1)	22.39
Fe_2O_3	(1)	n.d.
MnO	0.22	0.20
MgO	18.90	19.94
CaO	1.75	1.89
Na_2O	0.57	0.24
K_2O	0.034	0.04
P_2O_5	0.23	0.23
$H_2O(+)$	8.80	8.95
$H_2O(-)$	3.26	1.14
SO_3	2.38	0.90
S	0.49	(4)
S=	1.81(2)	(3)
C	1.91 (Total)	1.85
CO_2	n.d.	1.00
N	0.096	n.d.
	(5)	99.80
Total Fe	20.44	22.13
Total S	3.24_8	3.00

(1) See discussion in section - Wet Chemical Analysis.

(2) A calculated value. Total S -[S as SO_3 + elemental S]

(3) Sulfide sulfur included in FeS value.

(4) No elemental sulfur detected.

(5) No summation since values for FeS, FeO and Fe_2C_3 are not assigned.

(6) n.d. - Not determined.

TABLE 1b (atom %).—Comparison of chemical analyses Murchison on a volatile (C, H, N, O, S) free basis
(after Fuchs et al., 1973)

	Basis	
	This Work	Calculated from the Data of Jarosewich (197)
Fe	25.85	26.46
Ni	1.63_6	1.56_4
Co	0.071_3	0.071_5
Si	31.99	32.29
Ti	0.146	0.108
Al	2.82_2	2.81_5
Cr	0.37_4	0.42_2
Mn	0.21_8	0.18_8
Mg	33.12	33.04
Ca	2.20	2.25
Na	1.30	0.51_8
K	0.05_1	0.05_7
P	0.21_4	0.21_6

TABLE 2.—Electron microprobe analysis of Murchison matrix. (after Fuchs et al., 1973)

	1.	2.	3.	4.
SiO_2	23.4	26.2	23.4	25.9
Al_2O_3	3.1	3.5	3.1	3.4
Cr_2O_3	0.3	0.3	0.3	0.3
Fe_2O_3	-	-	7.6	8.4
FeO	34.1	38.2	27.3	30.3
MgO	15.1	16.9	15.1	16.7
CaO	0.9	1.0	0.9	1.0
MnO	0.2	0.2	0.2	0.2
NiO	1.5	1.7	1.5	1.7
H_2O	-	12.0	-	12.0
Sum	78.6	100.0	79.4	99.9
	Number of ions*			
Si	1.49		1.45	
Al	0.23	1.73	0.22	2.04
Cr	0.01		0.01	
Fe^{+3}	-		0.36	
Fe^{+2}	1.81		1.42	
Mg	1.43		1.39	
Ca	0.06	3.39	0.06	2.96
Mn	0.01		0.01	
Ni	0.08		0.08	
(OH)	4.54		4.49	

1. Average values for 40 spot analyses by J. Nelen, U.S.N.M., NiO is our datum.
2. Oxides in no. 1 recalculated to 88%, H_2O content is calculated from bulk H_2O^+ (see text).
3. 20% of Fe in no. 1 assigned as Fe^{+3}.
4. No. 3 recalculated to 88%, H_2O = 12.0%.

* Calculated to 9(O, OH).

The major phase in Murchison (77 vol. %) is the black matrix. Microprobe analysis of this matrix reveals a carbon content of 1.6-2.2 wt. % and a sulfur content of 1.6 - 4.1 wt. %.

The water content of the matrix has been estimated from the fraction of the water liberated above 105°C. This fraction was calculated from the amount of hydrogen liberated above this temperature. The total water is 12.1 wt. %, 8.8% is H_2O+.

The measured density of Murchison is 2.85. Assuming a density of 3.3 for the inclusions, Fuchs et al. (1973) report a density of the matrix of 2.71. Chemical analyses of the Murchison meteorite are shown in Tables 1a and 1b, Table 2 gives the results of an electron microprobe analysis of the Murchison matrix, and Table 3 shows the results of an electron microprobe analysis of the spinach green phase.

Twelve X-ray powder patterns (film) were taken of the black matrix from several areas on different specimens of Murchison (Table 4). Nine lines were common to these analyses, with impurities in some cases due to olivine or calcite. Two lines (intensity 3-5) were observed at 6.1 Å and 5.4 Å which were not mutually correlatable. The 6.1 Å line was removed without affecting the overall pattern with a five minute treatment of a 2% vital solution, and probably is due to an unidentified organic compound. Specimens showing the 5.4 Å line were found to contain several percent of two phases, one displaying massive amorphous and the other, fibrous textures. The fibrous phase exhibited the strong 5.4 Å line.

TABLE 3.—Electron microprobe analyses of "spinach" phase, Murchison meteorite. (after Fuchs et al., 1973)

	This Work		U.S.N.M.	
	1.	2.	3.	4.
SiO_2	28.0	28.0	23.4	23.4
Al_2O_3	2.6	2.6	3.7	3.7
Cr_2O_3	0.4	0.4	0.2	0.2
Fe_2O_3	-	2.3	-	2.0
FeO	29.3	27.3	36.8	35.0
MgO	19.9	19.9	11.6	11.6
CaO	-	-	0.3	0.3
MnO	-	-	0.1	0.1
Sum	80.2	80.5	76.1	76.3
	Number of ions*			
Si	1.70	1.68	1.61	1.59
Al	0.19	0.19	0.30	0.29
Cr	0.02	0.02	0.01	0.01
Fe^{+3}	-	0.10	-	0.11
	1.91	1.99	1.92	2.00
Fe^{+2}	1.49	1.37	2.11	1.99
Mg	1.80	1.79	1.19	1.18
Ca	-	-	0.02	0.02
Mn	-	-	-	-
	3.29	3.16	3.32	3.19
(OH)	4.00	4.00	4.00	4.00

1. Associated with Fo 99 in chondrule, E. Olsen analyst.
2. Recalculated, assuming 7% Fe as Fe^{+3}
3. Composition of associated olivine not determined. J. Nelen, analyst.
4. Recalculated, assuming 5% Fe as Fe^{+3}

* (OH) set to 4.00, formula calculated on the basis of 7 oxygen equivalents.

TABLE 4.—X-ray powder patterns* of the matrix material from the Murchison, Murray, and Mighei meteorites. (after Fuchs et al., 1973)

Murchison		Murray		Mighei		Assignments
d(Å)	I	d(Å)	I	d(Å)	I	
7.2	10	7.1	10	7.2	10	C
-	-	6.0	1	6.0	5	A.S.
5.4	1	5.4	1	5.4	1	U
4.7 }	Broad	4.7 }	Broad	4.7	1	C
4.3 }	Band	4.3 }	Band	4.51	2	A.S.
3.9	1	3.9	1	-	-	C
3.62	1	3.62	1	-	-	?
3.58	5	3.58	8	3.57	8	C
-	-	-	-	3.43	FT	?
-	-	-	-	3.33	FT	?
-	-	2.88	1	2.86	1	?
-	-	-	-	2.77	1	A.S.
2.70	2	2.70	3	2.69	2-	CM+CH
-	-	-	-	2.61	1	A.S.
2.53	8	2.54	6	2.53	10	CH
2.43	3	2.43	4	2.44	1	CM
2.30	1	2.29	1	2.36	1	C
2.16	4	2.16	3	2.16	6	CH
2.03	1	2.03	1+	2.03	1	CM
1.79	2	1.785	2	1.785	4	CH
-	-	1.68	2B	1.67	1B	C
1.57	3	1.575	3	1.57	3	C
1.54	3	1.540	2+	1.535	3	C
1.49	1	1.49	1	1.49	2	CH
1.44	1	1.44	1	1.438	1	C

*Fe radiation, Mn-filter, 114 mm Philips powder camera. Intensities are visual.

Abbreviations: B = broad; CM = monoclinic chamosite, CH = Hexagonal chamosite, C = lines common to CH and CM; A.S. = acid soluble. U = unidentified fibrous phase.

The septechlorite, chamosite and serpentine group was found to have x-ray properties similar to the nine lines common to all patterns. Chamosite was chosen as the best determination of the matrix material. In comparing the Murchison, Murray and Mighei x-ray patterns (Table 4), it was determined that the ratio of hexagonal to monoclinic chamosite was greatest for Mighei and least for Murray, Murchison having an intermediate value.

Heating experiments performed on Murchison matrix material revealed a decomposition of the matrix layer structure beginning at 340°C and being virtually complete at 450°C. At 240°C magnetite begins to form, becoming the major phase at 450°C. The poorly characterized fibrous phase decomposes at 245°C, forming a new phase, probably troilite (lines at 2.65, 2.06, 1.32 Å). Table 5 gives the results of this heating experiment, performed in vacuo in a sealed silica capillary.

Treatment of the matrix with warm concentrated phosphoric acid for 30 minutes removed a grid of matrix material, leaving behind raised features, suggesting the presence of at least two phases in the matrix.

Mineral Occurrances

The spinach green material seen in some inclusions is a layered silicate yielding 14 lines ascribed to a mixture of monoclinic and hexagonal polymorphs of chamosite, or in some cases, chamosite and serpentine, with other unidentified impurities. Table 3 contains an analysis of this phase present in a chondrule.

Olivine is present in all types of inclusions ranging from Fa 0 to Fa 85, both as homogeneous and zoned crystals.

TABLE 5.—X-ray powder patterns* of Murchison matrix material in an evacuated silica capillary following each stepwise heating period. (after Fuchs et al., 1973)

Not Heated		3.7 Days 245°C		7.7 Days 245°C		1.7 Days 340°C		5.8 Days 340°C		24 Days 340°C		12 Days 400°C		19 Days 450°C		33 Days 450°C		Phase
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	
7.2	10	7.1	10	7.1	10	7.1	10	7.1	10	7.1	8	7.1	8	7.4	2	-	-	C
5.4	3	5.4	1															(1)
				3.9	1			3.9	FT									C
3.58	7	3.58	8	3.58	7	3.58	7	3.58	7	3.58	6	3.58	3	3.60	FT	-	-	C
				3.33	FT							3.50	2	3.50	2	3.50	FT	?
				2.97	1	2.97	2	2.97	3	2.97	3	2.97	3	2.97	4	2.96	4	M
				2.85	1													?
2.70	2	2.70	1	2.70	2	2.70	1	2.70	FT	2.70	FT	-	-	-	-	-	-	CM+Cl
								2.62	FT	2.64	1	2.65	2	2.65	3	2.65	2	FeS
2.54	7	2.54	8	2.54	8	2.54	8	2.54	9	2.54	8	2.53	10	2.52	10	2.52	10	(2)
2.44	1	2.44	1	2.44	1	2.44	2	2.45	1	2.44	1	-	-	-	-	-	-	CM
2.17	2	2.17	2	2.16	2	2.16	2	2.17	2	2.16	2	2.16	2	-	-	-	-	CH
2.12	1													2.09	2	2.09	2	M
				2.04	1	2.05	2	2.05	2	2.05	3	2.06	3	2.06	3	2.06	2	FeS
1.79	FT	1.79	FT	1.79	FT	1.79	1	1.79	1	1.79	1	1.79	1	-	-	-	-	CH
						1.72	1	1.72	1	1.72	2	1.72	1	1.72	1	1.72	1	M
						1.61	FT	1.61	FT	1.61	1	1.61	2	1.62	4	1.61	3	M
1.57	3	1.57	3	1.57	2	1.57	2	1.57	2	1.57	2	1.57	2	-	-	-	-	C
1.54	2	1.54	2	1.54	1	1.54	1	1.54	1	1.53	1	1.53	FT	-	-	-	-	C
				1.48	1	1.48	1	1.48	FT	1.48	1	1.48	2	1.48	5	1.48	4	M
								1.31	FT	1.32	FT	-	-	1.32	1	1.32	1	FeS+
																1.092	3	M
																1.048	2	M
																0.856	1	$M\alpha_1$
																0.854	1	$M\alpha_2$

*Cu radiation, Ni-filter, 114 mm Philips powder camera. Intensities are visual.

Abbreviations: FT = faint trace; CM = monoclinic chamosite; CH = hexagonal chamosite; C = lines common to CM and CH; A.S. = unidentified acid-soluble phase; (1) = unidentified fibrous phase; (2) = line common to M and CH; M = Magnetite.

Both orthorhombic and monoclinic forms of the enstatite-bronzite series occur with no zoning noted. Compositions range from Fs 1 to Fs 50. X-ray patterns of the orthorhombic crystals show both the disordered and normal ordered patterns. Fragments of calcic pyroxene are rare but do occur in the matrix, with Fe /(Fe + Mg) ratios of 0.06 - 0.09. In some of the minute blue-white inclusions, diopside was identified.

Metal comprises only 0.03% in the bulk analysis, and is found mainly within some olivine grains, both in the white inclusions as well as in chondrules. Some grains were found in the black matrix or within the calcium pyroxene. The grains are ovate and smooth, the largest reported being 0.42 mm. Analyses of the metal are given in Table 6.

Of the sulfides, troilite was several times more abundant than pentlandite. The Ni content of the troilite ranges from 0.2 wt. % to 1.7 %, and is higher where mottling is apparent.

No phosphates were recorded, but schreibersite was found in a chondrule composed entirely of metal.

Polysynthetically twinned calcite commonly is observed. Calcite grains are present in all sections studied, principally occurring in the matrix, but also present in the X-ray patterns of some white inclusions. The calcite grains, which were pure $CaCO_3$, ranged in size from a few to 80 microns.

Calcium oxalate monohydrate ($Ca(C_2O_4).H_2O$) or whewellite, was found between the olivine grains in one white inclusion. At 230°C it decomposes to a hygroscopic anhydrous salt, and at 480°C forms $CaCO_3$ + CO.

Table 6.—Electron microprobe analyses of metal grains in Murchison
(after Fuchs et al., 1973)

Location of grain			Fe	Ni	Co	Cr	P	Sum
Four grains within single chondrule	1	Center	93.8	5.6	0.40	0.96	0.28	101.0
		Edge	"	"	"	0.85	"	100.9
	2		94.6	4.3	0.32	0.79	0.32	100.3
	3		94.0	4.0	0.32	0.80	0.32	99.4
	4		93.7	4.9	0.35	0.86	0.37	100.2
Two grains within single chondrule	1		90.8	7.4	0.41	0.69	0.29	99.6
	2		92.2	5.6	0.74	0.78	0.37	99.7
Six grains in black matrix	1		92.1	5.5	0.40	0.83	0.35	99.2
	2		93.5	5.0	0.35	0.64	0.37	99.9
	3		94.0	4.8	0.38	0.73	0.32	100.2
	4		93.6	4.8	0.35	0.49	0.36	99.6
	5		93.7	4.8	0.32	0.77	0.35	99.9
	6	Edge	93.1	6.3	0.42	0.20	0.31	100.3
		to Edge	92.0	7.0	0.43	0.55	0.32	100.3

Spinel, chromite, and magnetite were observed in the meteorite. The spinel occurs as inclusions within olivine grains and in white inclusions; chromite is found as fragments in the matrix and in white inclusions; magnetite spherules occur in the matrix and within troilite, occasionally. These spinel group minerals are present in trace amounts only (Tables 7a and 7 b).

The presence of lawrencite is inferred from the patchs of hydrated red iron oxide occurring on many freshly broken and fusion-crust-covered surfaces.

Microcrystalline hibonite needles ($CaAl_{12}O_{19}$) provides the intense blue centers of some of the white inclusions. Perovskite ($CaTiO_3$) was found in scattered euhedral crystals (2-4 microns) with diopside and spinel surrounding patches of hibonite.

Plates of gypsum as large as 40 microns in size were found on the surfaces of some hard specimens and, like the calcite, showed no cations other than calcium present above the 2% level in a microprobe scan, and is believed to be a preterrestrial phase.

The average composition of glass present was approximately 77% SiO_2, 14% Al_2O_3, 9% CaO, and less than 1% $Na_2O + K_2O$. Glass inclusions in single olivine crystals were analyzed with the results given in Table 8. Iron poor olivines contain glass with less than 0.3 wt. % FeO, and in the zoned iron-rich olivines, relatively FeO enriched glasses occur. The normative (wt. %) composition for the glasses in Table 8 is 60% anorthite, 27% diopside, and 13% silica.

The poorly characterized phases were both soft and exhibited a dull beige color in reflected light. Microprobe analysis of the massive phase yielded the following average weight percents, with ranges in parentheses:

Table 7a.—Electron microprobe analyses of chromites (after Fuchs et al., 1973)

	1	2	3	4	5	6	7	8	9
Cr_2O_3	47.4	46.8	47.1	60.2	48.9	51.4	41.9	50.3	49.2
Al_2O_3	17.3	17.7	18.5	3.2	15.7	10.7	22.3	14.0	14.2
V_2O_3	0.6	0.5	0.4	0.6	0.8	0.7	0.6	0.7	0.7
TiO_2	0.9	0.7	0.6	0.5	1.6	1.7	0.9	1.2	1.4
FeO	26.7	28.4	25.4	32.9	27.4	29.3	27.7	27.2	28.2
MgO	6.2	5.7	8.1	1.3	5.7	4.5	6.9	6.7	5.8
MnO	0.3	0.2	0.2	0.3	0.3	0.3	0.2	0.3	0.3
Sum	99.4	100.0	100.3	99.0	99.4	98.6	100.5	100.4	99.8
	Numbers of ions on the basis of 32(0)								
Cr	9.93	9.80	9.65	14.07	10.25	11.33	8.49	10.60	10.47
Al	5.40	5.52	5.65	1.12	4.90	3.52	6.73	4.40	4.51
V	0.13	0.11	0.08	0.14	0.18	0.15	0.12	0.14	0.15
Ti	0.18	0.14	0.12	0.11	0.32	0.35	0.17	0.24	0.29
Fe^{+2}	5.92	6.28	5.51	8.14	6.07	6.84	5.95	6.07	6.34
Mg	2.45	2.24	3.13	0.57	2.24	1.89	2.63	2.66	2.33
Mn	0.06	0.05	0.05	0.07	0.06	0.07	0.05	0.06	0.06
$R^{+3}+R^{+4}$	15.64	15.57	15.50	15.44	15.65	15.35	15.51	15.38	15.42
R^{+2}	8.43	8.57	8.69	8.78	8.37	8.80	8.63	8.79	8.73
Sum	24.07	24.14	24.19	24.22	24.02	24.15	24.14	24.17	24.15
	Redistribution of ions to allow for an assigned percentage of total Fe as Fe^{+++}								
$\%Fe^{+++}$	8.0	8.0	11.0	9.0	8.0	10.0	10.0	11.0	11.0
$R^{+3}+R^{+4}$	15.99	15.95	15.96	15.98	16.01	15.87	15.97	15.91	15.93
R^{+2}	7.89	8.01	8.01	7.95	7.83	8.02	7.93	8.03	7.94
Sum	23.88	23.96	23.97	23.93	23.84	23.89	23.90	23.94	23.87

Note to Table: The number of divalent ions exceeds the ideal number of 8 and the sum of the quadrivalent and trivalent ions is less than the ideal number of 16. This indicates that either ferrous or ferric ions are in 6-fold coordination. For illustrative purposes, we have recalculated each analysis assuming that from 8 to 11 wt. % of the total Fe may be present as Fe^{+3} but no case is made for its presence. The departure in the total number of cations from 24 may be the result of analytical error.

TABLE 7b.—Electron microprobe analyses of spinels
(after Fuchs et al., 1973)

	1	2	3	4	5	6
Al_2O_3	71.1	46.5	59.9	67.4	67.3	69.6
Cr_2O_3	0.7	25.4	12.8	2.6	2.1	0.7
TiO_2	0.3	0.3	0.3	0.2	0.2	0.2
FeO	0.1	10.9	2.5	0.6	0.6	0.5
MgO	28.8	18.3	25.7	27.5	28.1	28.3
CaO	n.d.	n.d.	n.d.	1.6	0.1	0.0
Sum	101.0	101.4	101.2	99.9	98.4	99.3
n	1.722	1.855	1.780	n.d.	n.d.	n.d.
a(Å)	8.091	8.182	8.135	n.d.	n.d.	n.d.
	Numbers of ions on the basis of 32(0)					
Al	15.78	11.75	13.95	15.34	15.46	15.73
Cr	0.10	4.30	1.99	0.39	0.33	0.12
Ti	0.05	0.05	0.05	0.03	0.04	0.03
Fe^{+2}	0.01	1.96	0.42	0.09	0.09	0.08
Mg	8.08	5.85	7.57	7.91	8.16	8.09
Ca	-	-	-	0.34	0.02	0.0
$R^{+3}+R^{+4}$	15.93	16.10	15.99	15.76	15.83	15.88
R^{+2}	8.09	7.81	7.99	8.34	8.27	8.17

Notes to Table 7 b

Nos. 1,2, and 3 are 50-120 μm grains from 3 different olivine-spinel white inclusions.

Compositions of associated olivines are: Fa_0(No. 1), Fa_{10} (No. 2), Fa_{2-7} (No. 3).

Nos. 4 and 5 are 6 μm grains inside of glass inclusion 1a and 1b resp. Table 8.

Composition of host olivine is $Fa_{0.6}$.

No. 6 is a 12 μm inclusion in $Fa_{0.3}$.

n.d. = not determined

Mn, Zr, K, Na are below background.

TABLE 8.—**Electron microprobe analyses of glass inclusions in olivine.** (after Fuchs et al., 1973)

Incl. No.	SiO_2	CaO	Al_2O_3	FeO	MgO	MnO	K_2O	Na_2O	TiO_2	Cr_2O_3	Sum
1a	48.2	17.0	27.4	0.2	6.7	0	0	0.01	0.9	0.2	100.6
1b	48.1	21.3	21.6	0.3	3.6	0	0	0.01	1.1	0.1	96.1
2	45.4	21.6	25.7	0.2	4.6	0	0	0.01	0.9	0.2	98.6
3	63.1	10.7	12.9	7.1	2.6	0.1	0	0.3	0.6	0.2	97.6
4a	45.4	22.9	25.2	0.1	3.3	0	0	0	1.0	0.2	98.1
4b	43.6	23.8	21.0	0.2	9.4	0.03	0	0	2.1	0.1	100.2
4c	54.7	17.3	25.0	0.1	1.6	0	0	0.2	0.3	0	99.2
5	44.9	20.4	28.0	0.2	3.8	0	0	0	0.9	0.2	98.4
6	53.1	17.4	23.7	0.2	4.0	0	0	0	0.6	0.3	99.3
7	49.4	21.1	24.1	0.1	3.7	0	0	0.03	0.6	0.1	99.1
8	74.2	9.0	8.7	2.0	2.2	0.1	0.2	1.4	0.4	0.2	98.4
9	57.3	17.4	17.3	0.1	7.5	0.03	0.1	0.5	0.5	0.3	101.0
10	47.7	20.9	24.6	0.2	3.7	0.03	0	0.03	0.8	0.3	98.3
11	53.7	12.8	16.5	6.8	1.7	0.1	0.4	1.8	0.8	0.03	94.6
Av.	52.1	18.1	21.6	1.3	4.2	0.03	0.05	0.3	0.8	0.2	98.7

Notes: (1) 1a and 1b are 2 separated inclusions in one olivine grain; 4a is a homogeneous inclusion which is isolated from the intergrowths of 4b and 4c in the same olivine grain; remainder are single inclusions in different olivine grains.

(2) The fayalite content (in mol. %) of host olivines is 0-1 except for the following: No. 3 (25-45), No. 8 (3-8), No. 11 (23-35).

S 17.6 (16-19), Fe 42.0 (37-45), Ni 6.1 (5.9 - 8.2), Cr 1.6 (1.4 - 2.5), C 0.2, P 0.3, O 31.0, summing to 99.7. A faint trace of Si appear in a wavelength scan.

Fisher (1972) in a fission track analysis of uranium in Murchison reported 13.5 ± 2.5 U ppb.

Johnson et al. (1973) plots the % Reflectance relative to MgO vs. wavelength for Murchison. (Fig.1).

Krahenbuhl et al. (1973) lists his and other results of neutron activation analyses for trace elements for Murchison and other carbonaceous chondrites (Table 9).

Table 9

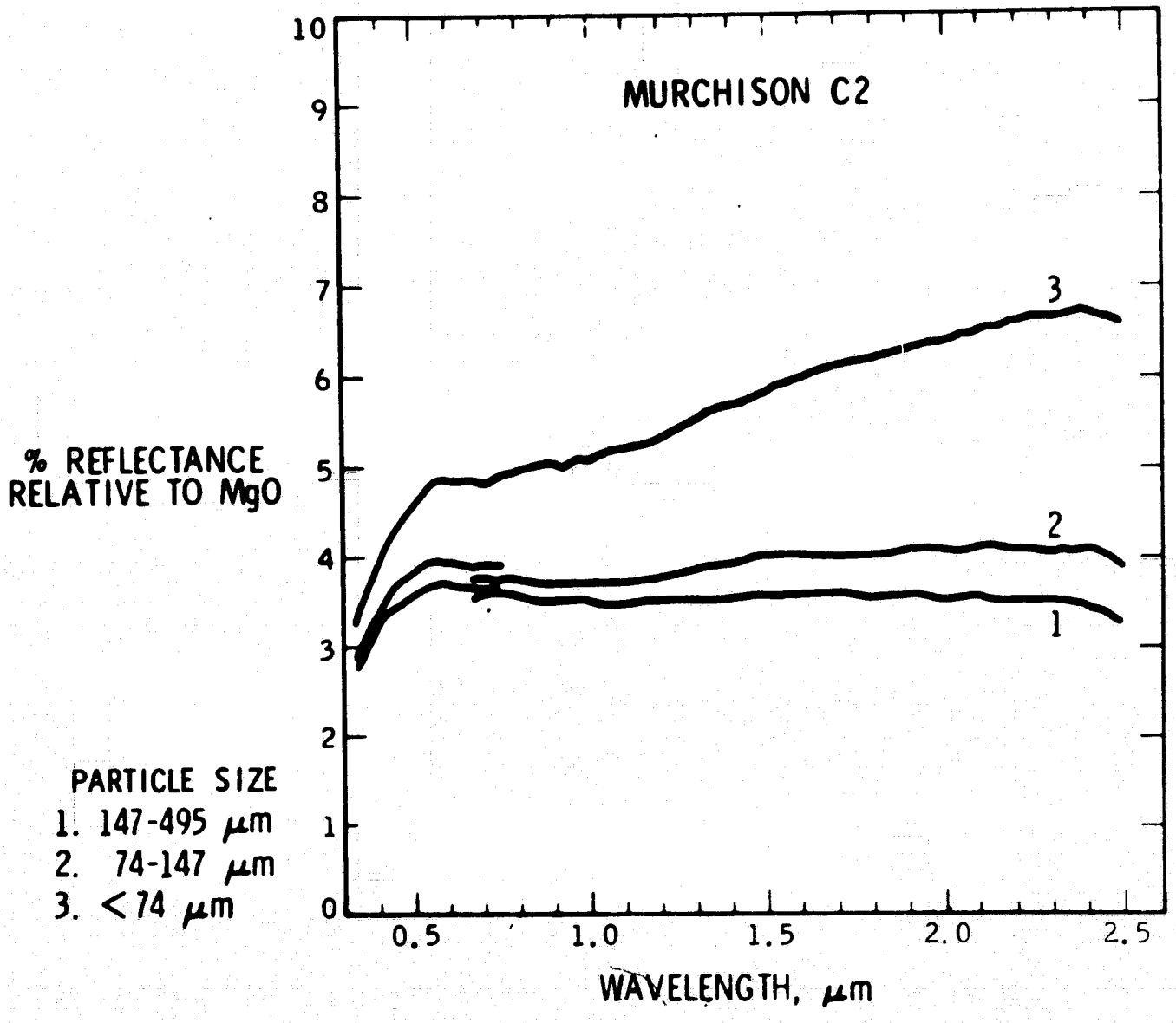
PPM

	Ir	Re	Au	Sb	Ge	Se	Te	AG	Br
Krahenbuhl, et al.	607	43.0	15.7	107	23800	11300	1800	172	(420)
Others	600		210 170 180						1500

In	Bi	Zn	Cd	Tl	Rb	Cs	U
46	64	175	379	84	1320	135	14.5
45			310	87			13.5

In an organic analysis of Murchison, Levy et al. (1973) reported the results of vaporization pyrolysis at 150°, 300°, and 430°C. 272 PPM

FIGURE 1



% REFLECTANCE RELATIVE TO MgO VS WAVELENGTH

organics were found consisting of N-alkanes, alkenes, aromatics, and thioaromatics from a Fischer-Tropsch Synthesis followed by partial equilibration of primary products.

At 300°C alkenes come off: ethelene, propylene, pentene as well as the aromatics, toluene and napthalene. Nonane and decane were observed, as well as N-undecane to be released at temperatures greater than 300°C.

At 430°C methane, ethylene, propylene, thioaromatics - thiophene (11) and 1- and 2- methylthiophene are released.

At 150°C toluene and undecane are released. The following come off at 430° C:

Isobutene	Toluene
Butane	2-Methylthiophene
1-Butane	3-Methylthiophene
2-Butene	Heptadiene
Pentene	Octene
Acetonitrile	Dimethylbenzene
Acetone	Dimethylthiophene
Pentadine	Stypene
Carbon disulfide	Nonane
Pentratriene	Trimethylbenzene
Hexene	Tetramethylbenzene
Hexadiene	Undecane
Heptene	Naphthalene
Dodecane	Tridecane

96% were found to be aromatics.

Table 10
(after Lawless, 1973)

Amino acids in the Murchison meteorite

1 Isovaline
2 α-Aminoisobutyric acid
3 D-Valine
4 Difunctional linear aliphatic (C_6)
5 L-Valine
6 N-Methylalanine
7 D-α-Amino-n-butyric acid
8 D-Alanine
9 Difunctional linear aliphatic (C_5)
10 L-α-Amino-n-butyric acid
11 L-Alanine
12 Difunctional linear aliphatic (C_5)
13 NH_3*
14 Difunctional linear aliphatic (C_5)
15 Difunctional linear aliphatic (C_5)
16 N-Methylglycine
17 N-Ethylglycine
18 D-Norvaline
19 L-Norvaline
20 Difunctional linear aliphatic (C_5)
21 Difunctional linear aliphatic (C_6)
22 D-β-Aminoisobutyric acid
23 L-β-Aminoisobutyric acid
24 β-Amino-n-butyric acid
25 Unknown†
26 D-Pipecolic acid
27 L-Pipecolic acid
28 Glycine
29 Difunctional cyclic
30 Difunctional cyclic
31 β-Alanine
32 Difunctional cyclic
33 Polyfunctional linear aliphatic
34 D-Proline
35 L-Proline
36 Difunctional linear aliphatic (C_5)
37 Unknown†
38 Unknown†
39 Difunctional linear aliphatic (C_5)
40 Unknown†
41 γ-Aminobutyric acid
42 D-Aspartic acid
43 L-Aspartic acid
44 Polyfunctional linear aliphatic
45 Polyfunctional linear aliphatic
46 Polyfunctional linear aliphatic
47 Polyfunctional linear aliphatic
48 Polyfunctional linear aliphatic
49 Unknown†
50 D-Glutamic acid
51 L-Glutamic acid
52 Unknown†

* Present in blank.

† Peaks labeled 'unknown' do not appear to be amino acids. Their identification awaits the use of high resolution mass spectrometry.

Gas chrcmatography combined with high resolution mass spectrometry of trimethyl silyl derivatives of Murchison by Folsome et al. (1973) showed three major groups of compounds:

1) 4 - Hydrox pyrimidines

2) N,N,C-alkyl-keto-hexahydropyrionidines

3) a heterogeneous class of possible pyrimidines.

Thirty-five amino acids were revealed in another study using gas chromatography combined with mass spectrometry by Lawless (1973) (Table 10).

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Summary of Individual Samples

Results from individual samples are as follows:

Montmorillonite - The sample is a calcium-sodium rich expendable clay mineral with minor amounts of quartz and illite. Even at the lowest temperature (150°C) there were obvious changes in the mineral structure and at 275°C the structural change was pronounced. Phase changes at both temperatures were accompanied by substantial water loss. There was no detectable change in the quartz or illite or in the fluid inclusions in the quartz and trace mineral grains.

Murchison meteorite - No changes were apparent in the major amounts of pyroxene and olivine. However, the chlorite or chamosite-like matrix mineral(s) underwent changes as evidenced by loss of some of the x-ray diffraction maxima and volatile loss.

Limonite - The limonite sample contains quartz, goethite and a small amount of a dioctahedral mica. Heat treatment at 150°C in vacuum resulted in production of a small amount of hematite and substantial loss of water and treatment at 275°C resulted in destruction of the goethite and formation of hematite. The quartz and mica do not appear to have been affected by either treatment. There were a few grains of chert and detrital quartz that did retain aqueous inclusions after the 275°C treatment and it is postulated that they probably reflect the environment of formation of the material that was weathered to yield the limonite. Thus, it is possible that, if any limonite were to be present in a Mars surface sample return, there would be information concerning the pre-limonite material retained following sterilization.

Hesperia soil - The Hesperia soil sample contains major amounts of quartz and feldspar which are not affected by either heat treatment. The clay mineral components do exhibit a slight change following heat treatment at 275°C - a sharpening of the illite (001) maximum and apparent elimination

of a mixed layer clay mineral component. Examination of the heated grains demonstrated that devitrification of glass (within some of the plagioclase grains) was not evident. It appears that these inclusions would yield important information concerning the composition of the glass, the temperature of crystallization and the petrogenesis to be expected from such melts.

W-1 - Analysis of the W-1 standard diabase suggests that mineralogical changes are minimal following sterilization.

General Conclusions

1. As anticipated, even low temperature dry heat sterilization will cause some mineralogical and chemical changes. These are mostly related to loss of volatiles, such as water.
2. There will be some problems with loss of volatile elements and isotopic fractionation of volatile elements as are suggested by the oxygen and lead data.

Recommendations

1. Dry heat sterilization temperatures should be kept as low as possible in order to preserve the maximum amount of inorganic science information.
2. Much of the sample information loss can be reconstructed if the sterilization history is precisely known and the effluent volatiles are collected or monitored. It is recommended that this be done if possible.
3. A Mars surface sample that has been sterilized at a temperature of as much as several hundred degrees centigrade is still of extreme scientific interest and importance. We recommend that the mission receive serious consideration even though sample sterilization may be required.
4. An extensive Mars sample analogue sterilization study does not appear to be justified until the exact conditions of the sterilization (if required) are known and there is better definitive information on the composition of the Martian surface.